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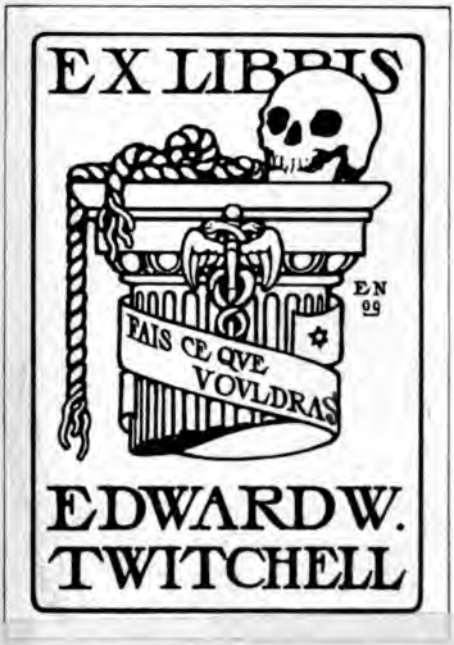

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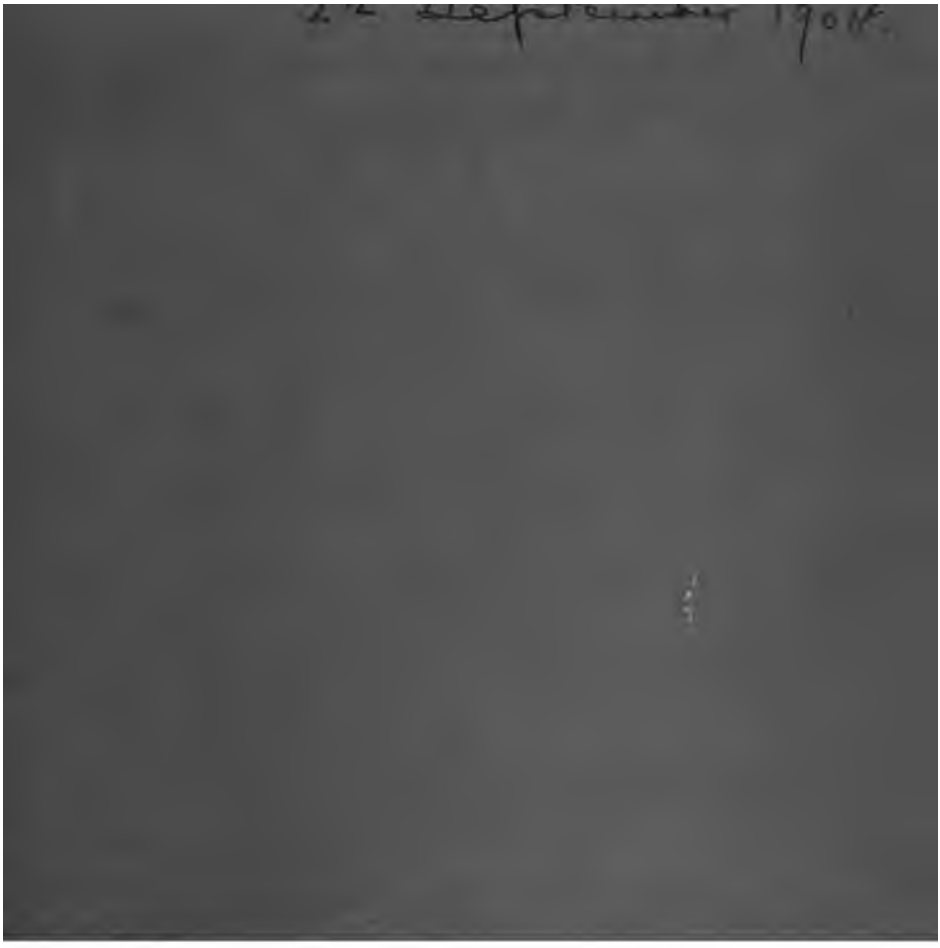

BLOXAM'S

CHEMISTRY

INORGANIC AND ORGANIC

BY THE SAME AUTHOR

LABORATORY TEACHING

OR

PROGRESSIVE EXERCISES IN PRACTICAL CHEMISTRY

Seventh Edition

BY HERBERT JACKSON

Demonstrator of Chemistry in King's College, London

[*In preparation*

CHEMISTRY
INORGANIC AND ORGANIC
WITH EXPERIMENTS

BY

CHARLES LOUDON BLOXAM

NINTH EDITION, REWRITTEN AND REVISED

BY

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PREFACE.

NOTWITHSTANDING the many competitors for public favour that have appeared during the past few years, the continued popularity of Bloxam's "Chemistry" indicates that its particular qualities are not to be met with in other works. Under the conviction that one of the chief claims of the book for attention is the constant reference to experiment, more especially in the earlier part, the Editors have retained this feature in the Ninth Edition.

The treatment of the Inorganic and Organic portions of the work in the one volume becomes increasingly more difficult, but this arrangement is undoubtedly convenient to those who use the book for the purpose of reference, and the temptation to divide the volume into two to admit of the fuller treatment of the Organic portion has been resisted. In the Editors' opinion the main objection to the condensed character of this part of the book is the necessary omission of many structural formulæ which are useful aids to students. It is believed, however, that sufficient explanation is given to enable the reader to construct the formulæ for himself; and the attempt to do so will prove far more instructive than the mere inspection of a printed formula.

A change has been made in the present edition in the order of treatment of the non-metallic elements, the place of Carbon having been changed so that its consideration occurs after that of the three other typical elements, Hydrogen, Oxygen, and Nitrogen.

Many of the old illustrations which had become obsolete have

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been removed from the work and several new illustrations, some in the division devoted to Organic Chemistry, have been introduced.

The plan adopted throughout several editions of making no division in the Organic portion between the treatment of the Fatty and Aromatic Compounds, being advantageous, has been again followed.

Due allowance being made for the time occupied in printing a book of this size, the Editors trust that their revision has brought the work up to date and that the present edition will be as favourably received as the two which have previously left their hands.

KING'S COLLEGE, LONDON.
August 1903.

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Yttrium	Y″	88.3	
Zinc	Zn″	64.9	
Zirconium	Zr^{iv}	89.9	

* The accent or index affixed to each symbol expresses the number of atoms of hydrogen for which the atomic weight of the element is *usually* exchangeable in chemical combinations. The numbers given are referred to the standard H = 1.

INTRODUCTION.

THE special province of Chemistry is the study of such changes in the properties of matter as are typified by the rusting of iron.

When the rust is examined it is found to be essentially different from the iron, which may be said to have changed its nature in becoming rust.

The melting of iron when it is very strongly heated is also a change in the nature of the metal, for the properties of a liquid are palpably different from those of a solid.

The two changes are, however, dissimilar in character; for the rust does not again become iron when left to itself, whereas the liquid iron again becomes solid when allowed to cool, and the cold mass in no way differs from the original iron.

Both phenomena are accompanied by an alteration of the iron from the grey, solid form in which it generally exists, but the phenomenon of rusting produces a change which is *permanent*, whilst that of liquefaction produces a change which is only *temporary*.

A distinction is generally drawn between these two kinds of change by calling the permanent kind a *chemical* change, and the temporary kind a *physical* change.

An instrument indispensable for the study of chemistry is the

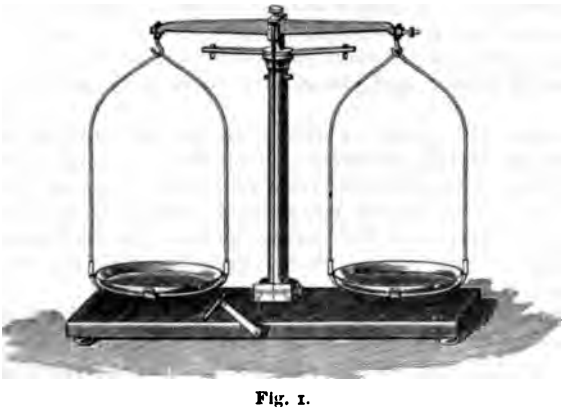


Fig. 1.

balance (Fig. 1)—a pair of scales sufficiently sensitive to show small differences of weight.

If a portion of iron be weighed before and after it has rusted, the iron, together with its coat of rust, will be found to be heavier than the original iron.

Since *matter*, in a chemical sense, is anything which possesses weight, the quantity of matter in the rust is greater than that in the iron. It must not be supposed that any matter has been *created* during the rusting. The matter which has now become attached to the iron has been acquired from the atmosphere, where it previously existed in the invisible, but none the less weighable, form of matter, the gaseous state.

Another common example of a chemical change is furnished by heating a lump of marble at a red heat. There is here no very conspicuous alteration in the appearance of the marble, although the structure of the piece is seen to have been somewhat modified. It can easily be shown, however, that there has been a permanent change wrought in the marble, for when the lump has cooled it is found to become hot again, and to crumble to powder when water is poured upon it; neither of these manifestations occurs when the original marble is wetted with water.

By weighing the marble before and after it has been heated, a loss of weight may be proved to have occurred during this chemical change—a quantity of matter has left the marble.

Here, however, there has been no *destruction* of matter; that which has left the marble has disappeared because it has been converted into the invisible or gaseous form, and has spread itself through the surrounding atmosphere.

By allowing iron to rust in a tightly corked bottle (containing air), and by heating marble in an apparatus designed to prevent the gas which is evolved from passing into the surrounding atmosphere, it can easily be demonstrated that neither the bottle nor the apparatus alters in weight during the rusting or heating.

A little reflection will show the reason for this. When an "empty" bottle is tightly corked there is enclosed in it a portion of the atmosphere, which is weighed with the bottle and remains unchanged until the cork is removed. If iron is also in the bottle, it rusts by attaching to itself a portion of the atmosphere present, and the atmosphere loses just as much matter as the iron gains during the process, so that the total amount of matter, and therefore of weight, in the bottle remains unaltered.

So, also, when the apparatus containing the marble is heated, the gas which leaves the marble is restrained from disseminating itself through the surrounding atmosphere and from no longer affecting the balance. When kept, as it were, on the balance-pan by being suitably caught, it is weighed with the rest of the marble, so that there is the same quantity of matter on the pan as there was before, and the total weight remains unaltered.

The above observations are concisely expressed in the definition of the principle of the *conservation of matter*:—In any space the total quantity of matter remains the same, although the matter may move from one part of the space to another or be transformed from one kind of matter into another. The special enclosure of the iron and the marble would be unnecessary for the above proof of the principle, were it possible to weigh the whole room in which the experiments are performed.

The two chemical changes which have been so far discussed are essentially different, in that the iron has had another kind of matter (the oxygen gas of the atmosphere) *added to* it, whilst the marble has had another kind of matter (the gas carbon dioxide) *separated from* it.

The first kind of change, the addition of two or more kinds of matter to each other, producing a third kind, is known as *chemical combination*. The latter, the separation of one kind of matter into two or more different kinds, is known as *chemical decomposition*.

It has been found that iron can undergo only the first kind of chemical change—it can only be converted into another kind of matter by chemical combination; iron cannot be decomposed. Much investigation has shown that this peculiarity of iron is shared by 76 other kinds of matter, so that all substances fall into two classes, namely:

Elements, or those substances which cannot be decomposed.

Compounds, or those substances which can be decomposed.

The substances in the latter class are, of course, much more numerous than the elements. They may be decomposed into other, simpler compounds, or into the elements of which they consist.

Thus, the first products of the decomposition of marble are lime (the solid referred to above as becoming hot when water is poured upon it), and carbon dioxide gas. Each of these, however, is itself a compound, and can be further decomposed (not easily by heat), the first into calcium and oxygen, the second into carbon and oxygen. These three substances—calcium, carbon, and oxygen—are not capable of decomposition, so far as we know.

The following list includes the various kinds of matter at present believed to be elements. It will be understood that the category is liable to both extension and contraction; for the discovery of new elements, the existence of which has been unsuspected, or the demonstration that what has heretofore been called an element is in reality a compound, may at any time necessitate an alteration of the list. The reason for the division of the elements into non-metals and metals will be given hereafter.

The *Non-Metallic Elements* are (20).

*Oxygen.	Sulphur.	*Fluorine.	*Argon.
*Hydrogen.	Selenium.	*Chlorine.	*Helium.
*Nitrogen.	Tellurium.†	Bromine.	*Krypton.
Carbon.		Iodine.	*Neon.
	Phosphorus.		*Xenon.
Boron.	Arsenic.†		
Silicon.			

* Gases at the ordinary temperature.

† Arsenic and tellurium are frequently classed among the metals, which they resemble in some of their properties.

The *Metals* are (56).

Cæsium.	Aluminium.	Zinc.	Copper.	Mercury.
Rubidium.	Gallium.	Nickel.	Bismuth.	Silver.
Potassium.	Germanium.†	Cobalt.	Lead.	Gold.
Sodium.	Zirconium.	Iron.	Thallium.	Platinum.
Lithium.	Thorium.	Manganese.	Tin.	Palladium.
Barium.	*Yttrium.	Chromium.	Titanium.	Rhodium.
Strontium.	*Erbium.	Cadmium.	Tantalum.	Ruthenium.
Calcium.	*Samarium.	Uranium.	Molybdenum.	Osmium.
Magnesium.	Scandium.	Indium.	Tungsten.	Iridium.
Beryllium.	Cerium.		Vanadium.	
	Lanthanum.		Antimony.†	
	Neodymium.			
	Praseodymium.			
	Niobium.			
	*Terbium.			
	*Ytterbium.			
	*Thulium.			

Many of these elements are so rarely met with, that they have not received any useful application, and are interesting only to the professional chemist. This is the case with the elements in the last column of the Table, p. 3, among the non-metallic elements, and with a large number of the metals.

The following list includes those elements with which it is important that the general student should become familiar, together with the symbolic letters by which it is customary to represent them, for the sake of brevity, in chemical writings :—

Non-Metallic Elements of practical importance (13).

Oxygen,	O	Sulphur,	S	Fluorine,	F
Hydrogen,	H			Chlorine,	Cl
Nitrogen,	N	Phosphorus,	P	Bromine,	Br
Carbon,	C	Arsenic,	As	Iodine,	I
Boron,	B				
Silicon,	Si				

Metallic Elements of practical importance (28).

Potassium,	K (*Kalium*)	Cadmium,	Cd
Sodium,	Na (*Natrium*)	Uranium,	U
Barium,	Ba	Copper,	Cu (*Cuprum*)
Strontium,	Sr	Bismuth,	Bi
Calcium,	Ca	Lead,	Pb (*Plumbum*)
Magnesium,	Mg	Tin,	Sn (*Stannum*)
Aluminium,	Al	Titanium,	Ti
Zinc,	Zn	Tungsten,	W (*Wolframium*)
Nickel,	Ni	Thorium,	Th
Cobalt,	Co	Cerium,	Ce
Iron,	Fe (*Ferrum*)	Antimony,	Sb (*Stibium*)
Manganese,	Mn	Mercury,	Hg (*Hydrargyrum*)
Chromium,	Cr	Silver,	Ag (*Argentum*)
		Gold,	Au (*Aurum*)
		Platinum,	Pt

* There is some doubt as to the elementary nature of these substances.
† Sometimes classed among the non-metals.

Although the 41 elements here enumerated are of practical importance, many of them derive their importance solely from their having met with useful applications in the arts. The number of elements known to play an important part in the chemical changes concerned in the maintenance of animal and vegetable life is very limited.

Elements concerned in the Chemical Changes occurring in Life.

Non-Metallic.		*Metallic.*	
Oxygen.	Sulphur	Potassium.	Aluminium.
Hydrogen.	Phosphorus.	Sodium.	Iron.
Nitrogen.		Calcium.	Manganese.
Carbon.	Chlorine.	Magnesium.	
Silicon.	Iodine.		

These elements will, of course, possess the greatest importance for those who study Chemistry as a branch of general education, since a knowledge of their properties is essential for the explanation of the simple chemical changes which are daily witnessed.

The student who takes an interest in the useful arts will also acquaint himself with the remainder of the 41 elements of practical importance, whilst the mineralogist and professional chemist must extend his studies to every known element.

By far the greater proportion of the various materials supplied to us by animals and vegetables consists of the four elements—oxygen, hydrogen, nitrogen, and carbon; and if we add to these the two most abundant elements in the mineral world, silicon and aluminium, we have the six elements composing the bulk of all matter.

It is computed that of the mineral matter of the earth's crust oxygen constitutes 50 per cent., silicon 25.3, aluminium 7.3, iron 5, calcium 3.5, magnesium 2.5, sodium 2.3, potassium 2.2, and hydrogen 1. No other element is present to a greater extent than 0.3 per cent.

The formation of a chemical compound consists in the combination of two or more elements, brought about by the inherent attraction of the elements for each other. This attraction varies between different elements. Whilst some combine with each other immediately they are brought in contact, others show no such tendency. In the sequel, the nature of *chemical attraction* will receive attention. It must here be stated that the phenomenon of combination has long been attributed to a force termed *chemical affinity:* thus the rusting of iron is said to consist in the formation of a compound of iron with oxygen, determined by the chemical affinity of these elements for each other.*

A characteristic of a chemical compound is homogeneity of structure. Pure compounds seldom exist in nature. The rock called granite, for example, is not a single chemical compound, but a mixture of chemical compounds, as, indeed, is rendered apparent by a merely superficial examination, when it is seen that there are three distinctly different substances in the granite. This at once stigmatises the rock

* For the sake of simplicity, no reference has been made to the necessity for the presence of other substances besides oxygen and iron for the formation of rust. It will be familiar to most readers that water is one of these essentials.

as a mixture, for it is never possible to see the elements in a compound. When the granite is powdered, a microscope is requisite to make its heterogeneous character visible, but by taking advantage of some essential difference between the properties of the three constituent substances—as, for instance, the different rates at which they sink in water—a separation, more or less perfect, may be effected.

No such differentiation of the parts of a lump of sugar can be detected. This is a pure compound, and is homogeneous, so that when it is powdered, every granule of it possesses the same properties as those of the whole mass—each will dissolve in water, will taste sweet, &c.

Thus, a *mixture* of elements or compounds is readily distinguished from a pure compound by the fact that each constituent of the mixture retains its individual properties, whereas in a pure compound the properties of its constituents (elements) are entirely obliterated.

Most natural substances consist of mixtures of compounds. The classification of the science of chemistry into *organic chemistry*, dealing with animal and vegetable substances, and *inorganic chemistry*, dealing with mineral substances, is based on the supposition, formerly held, that compounds produced through the operation of animal and vegetable life (such as sugar, starch, &c.) are essentially different from those which are, or have been, formed without the intervention of life. This classification is still adopted as convenient for the purposes of study.

It is the object of the chemist both to determine the constituents of every substance—a process termed *analysis*—and to build up every substance from its constituents—a process termed *synthesis*.

When these processes are directed merely to the determination of the nature or quality of the constituents, they are said to be *qualitative*, while when they take cognisance of the proportion which the constituents bear to each other, they are *quantitative—gravimetric* if the proportion by weight is considered, *volumetric* if the proportion is by volume.

In the early history of Chemistry, investigations were purely qualitative, and had they remained so the whole of chemical knowledge might be told in a dozen pages of this book. It was the use of the balance that revealed the very essence of the science—the fact that *every compound is of constant quantitative composition.*

Marble, chalk, and coral were early recognised by qualitative analysis to consist of the same compound mixed with small amounts of other substances. Afterwards, quantitative analysis showed that in each case the compound in question contains, by weight, 56 per cent. of lime and 44 per cent. of carbon dioxide.

Moreover, the same compound, now called calcium carbonate, was soon synthesised by bringing together lime and carbon dioxide made from other sources than any of the three minerals named; it was found that, whatever proportions of lime and carbon dioxide were used, the compound produced always contained no more and no less than 56 per cent. of the one and 44 per cent. of the other.

Thus, if 28 parts of lime were brought into contact with 72 parts of carbon dioxide, not 100 but 50 parts of calcium carbonate were formed; the 28 parts of lime combined with only 22 parts of carbon dioxide (the same ratio as 56 : 44) and 50 of carbon dioxide were left over, uncombined.

It is sufficiently remarkable that calcium carbonate from marble formed ages ago by solidification of a fused mass under great pressure, from chalk deposited during ages as mud from suspension in water, from coral built up by marine animals in our own day, and from material made in a few minutes in a laboratory, should have the same quantitative composition.

When a number of facts of this kind had been accumulated it became possible to assert that constancy of quantitative composition is *the* criterion by which a compound may be known. Any form of matter showing variation of composition cannot be a single compound.

For instance, a mass of chalk which has been wetted with water contains a considerable proportion of the latter, but one which varies with the source of the chalk; hence there is here no compound of chalk with water. On the other hand, lime from any source absorbs always 32 per cent. of its weight of water—the product is a compound.

Lime and carbon dioxide which have been spoken of as the constituents of calcium carbonate are only the *proximate*, not the *ultimate* constituents thereof. For each is capable of decomposition, though not easily by heat, into elements, the lime into calcium and oxygen and the carbon dioxide into carbon and oxygen. What is true of the combination of lime with carbon dioxide is true of that of calcium or carbon with oxygen; wherever or however these compounds are obtained, they contain their constituent elements always in the same proportion.

A collection of observed facts in agreement with each other enables the investigator to formulate a law of Nature which remains valid so long as newly discovered facts do not contradict it. In this case the law, which may be regarded as the sheet-anchor of Chemical science, is known as—

The Law of Constant Proportions.—Every compound contains its constituent elements always in the same proportion, from whatever source the compound may be obtained.

An attempt to explain this and other similar laws which the student will learn presently, led Dalton, a century ago, to the hypothesis as to the structure of matter, called the *atomic theory*. The facts and arguments which justify this hypothesis will be referred to hereafter. It is, however, essential that the student should attempt to grasp the fundamental conception on which the theory is based before embarking on a study of the relationships between the elements.

The fundamental conception is this:—When matter is submitted to a process of subdivision, a certain fineness will ultimately be attained beyond which disintegration will be impossible; in other words, *any given mass of matter consists of a number of particles, each of which cannot be divided.* Thus, when a piece of marble has been ground to powder, the single particle has become a large number of particles. Now, by the hypothesis stated above, could the process of grinding be perfected, a stage would be reached when it would be impossible to further increase the number of these particles, for each would be indivisible. The ultimate particle of marble would then have been attained. These ultimate particles of matter are called *molecules.*

But it has been already stated that when marble is heated, it is decomposed into lime and carbon dioxide, so that it is possible to sub-

divide marble by a process other than mechanical grinding; but the product is no longer marble. What is true of the lump of marble should be true also of its mechanically indivisible particle, or molecule. *The molecules of marble can still be divided by decomposing them.*

It is highly probable that the molecules of marble, were they separated, would be found to be invisible. The smallest visible particle of marble is probably an aggregate of many molecules. It is not possible to render marble invisible, because we have no means for moving the molecules which make up these aggregates appreciably further from each other. This is because the method usually adopted for the purpose of separating molecules from each other—namely, the application of heat—decomposes the molecules of marble.

There are many substances, however, the molecules of which are not decomposed by a moderately intense heat, and are moved so far apart from each other by the application of this agency, that the whole mass becomes invisible. Water is a familiar example, steam being invisible until it is so far chilled that the separated molecules have come together again to form visible particles. Gases which remain such at the ordinary temperature require to be very much chilled in order to bring their molecules sufficiently close to each other to form visible particles—in other words, to convert the gas into a liquid.

There are several methods for subdividing a substance without decomposing it, of which two (mechanical grinding and the application of a moderate heat) have been quoted. Such methods may be called physical methods of subdivision, inasmuch as they do not produce a chemical change.

A MOLECULE may now be defined as the ultimate particle of a compound or element, divisible only by chemical change.

Inasmuch as an element cannot be decomposed, its molecules must be incapable of any further division such as that possible for the molecule of a compound like marble. This is true when the molecules of the element exist by themselves; there is no evidence to show that the molecules of oxygen, for instance, can be divided so long as the oxygen exists by itself in an uncombined condition.

There is excellent evidence, however, that the molecules of many compounds contain half the quantity of oxygen that the molecule of this element contains. It must be admitted, therefore, that the oxygen molecule consists of two parts, which can only be separated from each other when the molecule enters into combination. The same argument applies to other elements, the molecules of the majority of which consist of parts, although several have no parts.

These parts of elementary molecules are indivisible either by physical or chemical methods; they are therefore the true *indivisibles* or *atoms*.

An ATOM may be defined as the smallest particle of an element existing in a molecule, indivisible by any means.

A consideration of the above definition, together with that given for a compound, will show that to speak of the atom of a compound would be a contradiction of terms.

What has been said above as to the fundamental conception of the atomic theory may be thus summarised. Matter is not capable of infinite subdivision, but consists of particles which are indivisible and are called atoms; these have no separate existence, but occur in combination

with each other to form molecules, which are the smallest particles capable of separate existence. When the atoms thus united are of the same kind, the molecule is that of an element; when they are of different kinds the molecule is that of a compound. When compound molecules are decomposed the atoms of the constituent elements are momentarily liberated, but immediately recombine to form new molecules. Each atom of the same element has the same weight; but the atoms of different elements have different weights.

How Dalton applied this conception to explain the laws of chemical combination is fully set forth in the chapter on General Principles.

It is agreed among chemists that the symbol for an element shall represent one atom, and a certain number of parts by weight, of the element. This figure is termed the *atomic weight* of the element, and is believed to be the number of times that an atom of the element is heavier than an atom of the gaseous element hydrogen, which is said to weigh 1. It is an abstract number, and may represent any units of weight. Thus, the symbol O means one atom of oxygen and 16 unit weights of oxygen—it may be 16 grains, 16 lbs., 16 grams, &c.

Since the atomic theory does not admit the existence of the atom of a compound, a compound cannot have an atomic weight.

The *molecular weight* of either an element or a compound is the number of times that the molecule is heavier than that of hydrogen, the molecule of which is said to weigh 2.

The molecular weight of a substance is ascertained by doubling the number of times that a volume of the substance in the form of vapour or gas is heavier than an equal volume of hydrogen, weighed at the same temperature and pressure.* This value is known as the *vapour density*† of the gas, and is determined by weighing a stoppered globe (such as that shown in fig. 50) of known weight, first when it is full of hydrogen, and then when it is full of the vapour or gas whose vapour density is to be determined; obviously, the vapour density will be the quotient,

$$\frac{\text{weight of (globe + gas)} - \text{weight of globe}}{\text{weight of (globe + hydrogen)} - \text{weight of globe.}}$$

Hence the MOLECULAR WEIGHT of an element or compound is twice the number of times that a volume of it in the state of gas is heavier than an equal volume of hydrogen weighed at the same temperature and pressure.

As the molecule of an element contains only atoms of the same kind, each having the same atomic weight, the molecular weight of the element must be a multiple of the atomic weight by 1, 2, 3, &c., accordingly as the molecule contains 1, 2, 3, &c., atoms.

Now the molecule of a compound can never contain less than one atom of any of its constituent elements because an atom cannot be divided. Hence the molecular weight of a compound can never contain

* It will be remembered that gases expand in volume when heated or when submitted to a reduced pressure; hence a given volume of gas never has the same weight unless its temperature and pressure are the same each time it is weighed (except in the rare event of a diminished temperature compensating for a diminished pressure).

† This term is used because the majority of substances must, like water, be vaporised by heat before they are in the gaseous state.

less than one atomic weight of each of the constituent elements, though it may contain more.

It is possible, therefore, to define the ATOMIC WEIGHT of an element as the smallest weight of it found in one molecular weight of any of its compounds.

For example, by the method described above carbon dioxide is found to have the vapour density 22, consequently its molecular weight is 44. Now analysis shows that 44 parts by weight of carbon dioxide contain 12 parts by weight of carbon, and as this is the smallest weight of this element that occurs in one molecular weight of *any* of its compounds, it is the atomic weight.

When the molecule of an element contains only one atom the symbol for the element represents both the atom and the molecule; thus Hg means both a molecule and an atom of mercury because the molecules of this element are *monatomic*. On the other hand, the molecules of hydrogen and oxygen are H_2 and O_2 respectively, these elements having *diatomic* molecules. Phosphorus is an element having *tetratomic* molecules, expressed by the symbol P_4. Such molecular symbols represent twice or four times the atomic weight; thus $O_2 = 16 \times 2 = 32$ parts by weight. $P_4 = 31 \times 4 = 124$ parts by weight.

It follows from what was said above as to the method of ascertaining the molecular weight, that if the volume of one unit weight of hydrogen be called unit volume, the molecular weight of any gas, expressed in the same units, must be called two volumes. For example, if the volume occupied by one *gram* of hydrogen be called one volume, 32 *grams* of oxygen will occupy two volumes. The symbol for any molecule, therefore, represents two volumes of the substance in the state of gas.

The symbol for a compound is called a *formula*, and represents the molecule of the compound, which consists of atoms of its constituent elements united together, so that the formula is the symbols for these atoms written side by side; thus, HCl represents a molecule of a compound of hydrogen with chlorine; HCN, the molecule of a compound of hydrogen, carbon, and nitrogen; and each represents two volumes of the compound in the state of gas. When analysis shows that there are 2, 3, or 4 atomic weights, and therefore atoms, of the same element present in one molecule of the compound, this is expressed by writing 2, 3, or 4 after the symbol for the element. Thus, H_2SO_4 represents a compound whose molecule contains two atomic weights or atoms of hydrogen, one atomic weight or atom of sulphur, and four atomic weights or atoms of oxygen.

Thus the number of parts by weight expressed by the formula for a compound is the sum of the atomic weights of the elements present; HCl means $1 + 35.5 = 36.5$ parts by weight of hydrogen chloride; HCN means $1 + 12 + 14 = 27$ parts by weight of hydrogen cyanide; H_2SO_4 means $(1 \times 2) + 32 + (16 \times 4) = 98$ parts by weight of sulphuric acid.

The mere contact or mixture of substances is expressed by the sign +; thus $H_2 + Cl_2$ implies that a molecule of hydrogen has been brought into contact with a molecule of chlorine.

From the point of view of the atomic theory, chemical combination is regarded as consisting in the exchange of atoms in one molecule for those in another, when the molecules are brought in contact.

For example, chemical combination occurs between hydrogen and chlorine, to form hydrochloric acid, the change being represented by the *chemical equation* $H_2 + Cl_2 = 2HCl$, which implies that the molecules of hydrogen and chlorine exchange atoms.

It will be seen from the statements made above, that this equation also implies that 2 parts by weight or 2 vols. of hydrogen and 35.5×2 parts by weight or 2 vols. of chlorine, yield 36.5×2 parts by weight or 4 vols. of hydrochloric acid.

It must be remembered that a chemical equation is only a short mode of expressing the result of an experiment, and cannot be used, like a mathematical equation, to effect the solution of a problem.

A chemical equation may be written to express what is likely to be the result of the action of different molecules upon each other, but it has no value until verified by experiment.

Chemical decomposition is the separation of the atoms composing a molecule, which must precede the formation of a new molecule. Thus, the decomposition of steam by a very high temperature is expressed by the equation $2H_2O = 2H_2 + O_2$, which conveys the information that two molecules or 36 parts by weight or 4 vols. of steam have suffered chemical decomposition, and have formed two molecules or 4 vols., or 4 parts by weight of hydrogen, and one molecule or 2 vols., or 32 parts by weight of oxygen.

Chemical changes are always attended by evolution or absorption of heat. As a general rule, the formation of compound molecules from elementary molecules evolves heat, whilst the formation of elementary molecules from compound molecules absorbs heat. Hence it will be found that the application of heat is generally required for the commencement of chemical change, in order to effect that separation of atoms from their molecules which must precede every chemical transformation of matter. When any chemical change appears to occur without any change of temperature being observed, it is because the total heat absorbed in the destruction of the original molecules is equal to the total heat evolved in the construction of the new molecules.

The formation of water by the chemical combination of hydrogen and oxygen consists in the separation of the atoms which compose the oxygen molecule, and of those composing two hydrogen molecules, an atom of hydrogen from each hydrogen molecule uniting with an atom of oxygen from the oxygen molecule, as expressed in the equation, $OO + HH + HH = HHO + HHO$. Here, it is evident that the conversion of a molecule of oxygen into water is effected by the exchange of each of its oxygen atoms for two hydrogen atoms.

Since hydrogen is taken as the chemical standard or unit, and one atom of oxygen is exchangeable for, or combines with, two atoms of hydrogen, oxygen is said to be *divalent* or *diad*, often expressed by writing it thus, O″. The atoms of some elements are exchangeable for, or combine with, three atoms of hydrogen, and are said to be *trivalent* or *triad*‴; others for four, *quadrivalent* or *tetrad*^{iv}, or for five, *quinquivalent* or *pentad*^{v}, and so on.

A convenient classification, according to *valency*, is thus arrived at, which is liable, however, to a great number of exceptions.

Monads—Br, Cl, F, I, K, Ag, Na.

Diads—Ba, Cd, Ca, Co, Cu, Fe, Pb, Mg, Mn, Hg, Ni, O, Sr, S, Zn.

Triads—Al, Sb, As, Bi, B, Cr, Au, N, P.

Tetrads—C, Pt, Si, Sn.

In studying the properties of bodies, a distinction must be drawn between physical and chemical properties. The physical properties are those in which either the *mass* or the *molecules* are alone concerned, whilst the chemical properties concern the *atoms*. Thus, the condition whether solid, liquid, or gas, the colour, odour, taste, hardness, relative weight (or specific gravity), would come under the head of physical properties. For a solid, the geometrical form of its crystal and the temperature at which it melts are important for identification; and for a liquid, the temperature at which it boils.

Chemists use the *metric system* of weights and measures. It will be remembered that the unit of weight in this system is one *gram*, and that the unit of capacity is that volume which one gram of water occupies at 4° C. (at which temperature a given weight of water has a smaller volume than at any other temperature); this unit of volume is called a *cubic centimetre*. One thousand cubic centimetres make 1 *litre*. One gram is equivalent to 15.43 grains, and one litre is equivalent to 1.76 pint. One *metre* or 100 *centimetres* or 1000 *millimetres* = 39.37 inches.

INORGANIC CHEMISTRY.

CHEMISTRY OF THE NON-METALLIC ELEMENTS AND THEIR COMPOUNDS.

THE ELEMENTS OF WATER.

1. Until the latter half of the eighteenth century, water was regarded as an elementary form of matter. It was first resolved into its constituent elements, hydrogen and oxygen, by subjecting it to the influence of the *voltaic current*, which decomposes or *analyses* the water by overcoming the chemical attraction by which its elements are held together.

An arrangement for this purpose is represented in Fig. 2.

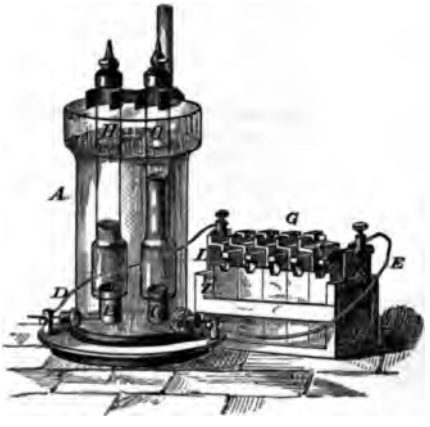


Fig. 2.—Electrolysis of water.

The glass vessel A contains water, to which a little sulphuric acid has been added to increase its power of conducting electricity, for pure water conducts so imperfectly that it is decomposed with great difficulty. B and C are platinum plates bent into a cylindrical form, and attached to the stout platinum wires, which are passed through corks in the lateral necks of the vessel A, and are connected by binding screws with the copper wires D and E, which proceed from the galvanic battery G. H and O are glass tubes with brass (or glass) caps and stop-cocks, and are enlarged into a bell-shape at their lower ends for the collection of a considerable volume of gas. These tubes are filled with the acidified water by sucking out

the air through the opened stop-cocks; on closing these, the pressure of the atmosphere will, of course, sustain the column of water in the tubes. G is a Grove's battery, consisting of five cells or earthenware vessels (A, Fig. 3) filled with

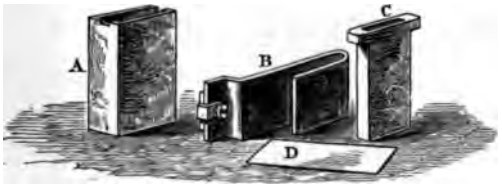


Fig. 3.

Fig. 4.

diluted sulphuric acid (one measure of oil of vitriol to four of water). In each of these cells is placed a bent plate of zinc (B), which has been *amalgamated* or rubbed with mercury (and diluted sulphuric acid) to protect it from corrosion by the acid when the battery is not in use. Within the curved portion of this plate rests a small flat vessel of unglazed earthenware (C), filled with strong nitric acid, in which is immersed a sheet of platinum-foil (D). The platinum (D) of each cell is clamped, at its upper edge, to the zinc (B) in the adjoining cell (Fig. 4), so that at one end (P, Fig. 2) of the battery there is a free platinum plate, and at the other (Z) a free zinc plate. These plates are connected with wires D and E by means of the copper plates L and K, attached to the ends of the wooden trough in which the cells are arranged. The wire D (Fig. 2), which is connected with the last *zinc* plate of the battery, is often called the "*negative* pole," whilst E, in connection with the last *platinum* plate, is called the "*positive* pole."

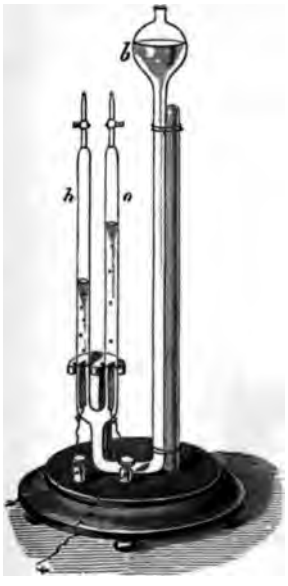


Fig. 5.—Electrolysis of water.

When the connection is established by means of the wires D and E with the "electrolytic cell" (A), the "galvanic current" is commonly said to pass along the wire E to the platinum plate C, through the acidified water in the electrolytic cell, to the platinum plate B, and thence along the wire D back to the battery.

Since the electricity travels into and out of the electrolytic cell by the plates B and C, these are called the *electrodes* (ἤλεκτρον, amber—root of electricity; ὁδος, a way). The plate C, or way into the cell, is called the *anode* (ανα, towards; ὁδος); the plate B, or way out of the cell, is the *cathode* (κατα, away from: ὁδος).

Another form of apparatus for this experiment is shown in fig. 5. The water displaced by the gases accumulating in the tubes *h*, *o*, collects in the bulb *b* upon the longer branch, and exerts the pressure necessary to force the gases out when the stop-cocks are opened. The stop-cocks, being made of glass, are not corroded by the acid.

2. During this "passage of the current" (which is only a figurative mode of expressing the transfer of the electric influence), the water intervening between the plates B and C is decomposed, its hydrogen being attracted to the plate B (negative pole or cathode), and the oxygen to the plate C (positive pole or anode). The gases can be seen adhering in minute bubbles to the surface of each plate, and as they

increase in size they detach themselves, rising through the acidified water in the tubes H and O, in which the two gases are collected.

Since no transmission of gas is observed between the two plates, it is evident that the H and O separated at any given moment from each plate do not result from the decomposition of one particle of water, but from two particles, as represented in Fig. 5, where A represents the particles of water lying between the plates P and Z before the "current" is passed, and B the state of the particles when the current has been established. P is (the anode) in connection with the last platinum plate of the battery, and Z is (the cathode) in connection with the last zinc plate.

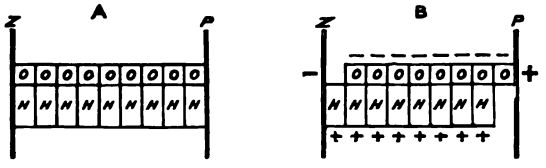


Fig. 6.

The signs + and – made use of in B refer to a common mode of accounting for the decomposition of water by the battery, on the supposition that the oxygen is in a negatively electric condition, and therefore attracted by the positive pole P; whilst the hydrogen is in a positively electric condition, and is attracted by the negative pole Z.

In the foregoing explanation, the part played by the sulphuric acid has been omitted for the sake of simplicity. Pure water could not be decomposed unless by a very much stronger battery. For a discussion of the part played by the sulphuric acid the reader must refer to the chapter on General Principles.

The decomposition of compounds by galvanic electricity is termed *electrolysis.** When a compound of a metal with a non-metal is decomposed in this manner, the metal is usually attracted to the (negative) pole in connection with the zinc plate of the battery, whilst the non-metal is attracted to the (positive) pole connected with the platinum plate of the battery.

Hence the metals are frequently spoken of as *electro-positive* elements, and the non-metals as *electro-negative.*

3. If the passage of the "current" be interrupted when the tube H has become full of gas, the tube O will be only half full, since *water is a compound of hydrogen and oxygen in the proportion of two volumes of hydrogen to one volume of oxygen.*† When the wider portions of the tubes (fig. 2) are also filled, the two gases may be distinguished by opening the stop-cocks in succession and presenting a burning match. The hydrogen will be known by its kindling with a slight detonation and burning with a very pale flame at the jet; whilst the oxygen will very much increase the brilliancy of the burning match, and if a spark

* Ἤλεκτρον, amber—root of *electricity*; λύω, to loosen.

† The volume of the oxygen is always found to be slightly less than one-half the volume of the hydrogen in this experiment, both because the solubility of oxygen in water is rather greater than that of hydrogen, and because a small proportion of the oxygen is evolved in the condition of ozone, which occupies only two-thirds of the volume occupied by an equal weight of oxygen (see Ozone).

left at the extremity of the match be presented to the oxygen, the spark will be kindled into a flame.

A volume of oxygen weighs 16 times as much as an equal volume of hydrogen, so that if one volume of hydrogen be said to weigh one part by weight, one volume of oxygen will weigh 16 parts by weight. But in water the proportion of hydrogen to oxygen is 2 volumes : 1 volume. Therefore the proportion by weight of these two elements in the water must be 2 : 16, or *water is a compound of hydrogen and oxygen in the proportion of 2 parts by weight of hydrogen to 16 parts by weight of oxygen.* Since the atom of oxygen is believed to weigh 16 times as much as the atom of hydrogen, the simplest view of the composition of the molecule of water is that it contains 2 atoms of hydrogen and 1 atom of oxygen; its formula may therefore be represented as H_2O.

4. The decomposition of water by electrolysis must be compared with a like experiment in which the compound decomposed is one of hydrogen with the element chlorine, a gas called *hydrogen chloride.* A solution of this gas in water, commonly known as *hydrochloric acid,* yields *equal volumes* of hydrogen and chlorine when electrolysed.

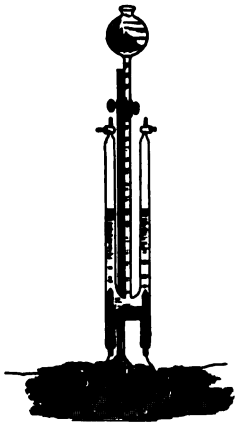


Fig. 7.

The apparatus represented in Fig. 5 requires a little alteration when it is to be used for the electrolysis of hydrochloric acid, and generally takes the form shown in Fig. 7. As chlorine attacks platinum, the electrodes are of carbon, which cannot be sealed in glass but must pass through corks. Strong hydrochloric acid is poured into the bulb until both limbs are filled with the acid : the stop-cocks are left open and the wires from the electrodes are connected with the poles of a battery of five or six Grove's cells. The gases are allowed to escape until the liquid is saturated with chlorine and cannot dissolve any more, this gas being sufficiently soluble in water to vitiate the experiment. The stop-cocks are then closed and the gases allowed to collect. The proportion of chlorine is always too small, owing to the difficulty of saturating the liquid with it. By dissolving as much common salt in the hydrochloric acid as it will take up, a better result is obtained.

The chlorine is evolved at the electrode connected with the platinum of the battery (the anode). It will be recognised by its greenish-yellow colour and pungent odour.

A volume of chlorine weighs 35.5 times as much as an equal volume of hydrogen, so that *hydrogen chloride is a compound of hydrogen and chlorine in the proportion of 1 part by weight of hydrogen to 35.5 parts by weight of chlorine.* The atom of chlorine is believed to weigh 35.5 times as much as that of hydrogen, hence a molecule of hydrogen chloride may be regarded as a compound of 1 atom of hydrogen with 1 atom of chlorine, represented by the formula HCl.

It will be noticed that—

1 vol. chlorine unites with 1 vol. hydrogen.

1 vol. oxygen „ „ 2 vols. „

Later it will be seen that 1 vol. of the element nitrogen unites with

3 vols. of hydrogen, and there is excellent evidence that if carbon, which is a solid very difficult to vaporise, could be obtained as a gas, 1 vol. of it would combine with 4 vols. of hydrogen. No element is known, 1 vol. of which combines with more than 4 vols. of hydrogen.

Here is an important basis for classification of the elements, for all those that combine with hydrogen belong to one of the above four classes, while the rest may be referred to the same classes as will be explained presently and as has been indicated at p. 11.

5. Another method of effecting the decomposition of water by electricity consists in passing a succession of electric sparks through steam. It is probable that in this case the decomposition is produced rather by the intense heat of the spark than by its electric influence.

For this purpose, however, the galvanic battery does not suffice, since no spark can be passed through any appreciable interval between the wires of the battery—a fact which electricians refer to in the statement that, although the *quantity* of electricity developed by the galvanic battery is large, its *tension* or *pressure* is too low to allow it to

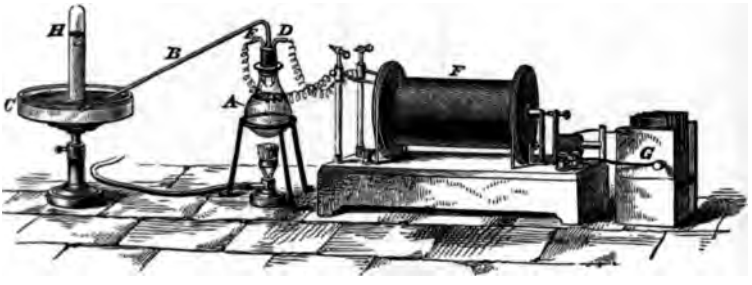


Fig. 8.—Decomposition of steam by electric sparks.

discharge itself in sparks like the electricity from the machine or from the induction coil, which possesses a very high tension, though its quantity is small.

The most convenient instrument for producing a succession of electric sparks is the *induction-coil*, in which a current of low tension, sent from a weak battery through a coil of stout wire and back to the battery, induces or excites a current of high tension in a coil of thin wire of great length, wound outside the thick coil. This current is capable of discharging itself in sparks, such as are obtained from the electrical machine.

Fig. 8 represents the arrangements for exhibiting this experiment.

A is a half-pint flask furnished with a cork in which three holes are bored; in one of these is inserted the bent glass tube B, which dips beneath the surface of the water in the trough C.

D and E are glass tubes, in each of which a platinum wire has been sealed so as to project about an inch at both ends of the tube. These tubes are thrust through the holes in the cork, and the wires projecting inside the flask are made to approach to within about $\frac{1}{8}$ of an inch, so that the spark may easily pass between them.

The flask is somewhat more than half filled with water, the cork inserted, and the tube B allowed to dip beneath the water in the trough, the wires in D and E being connected with the thin copper wires passing from the induction-coil F, which is connected by stout copper wires with the small battery G.

The water in the flask is boiled for about fifteen minutes, until all the air contained in the flask has been displaced by steam. When this is the case, it will be found that if a glass test-tube (H) filled with water be inverted* over the orifice of the tube B, the bubbles of steam will entirely condense, with the usual sharp rattling sound, and only insignificant bubbles of air will rise to the top of the test-tube. If now, whilst the boiling is still continued, the handle of the coil (F) be turned so as to cause a succession of sparks to pass through the steam in the flask. large bubbles of incondensable gas will accumulate in the tube H. This gas consists of the hydrogen and oxygen gases in a *mixed* state, having been released from their *combined* condition in water by the action of the electric sparks. The gas may be tested by closing the mouth of the tube H with the thumb, raising it to an upright position, and applying a lighted match, when a sharp detonation will indicate the re-combination of the gases.†

It has long been known that a very intense heat is capable of decomposing water. The temperature required for the purpose is below the melting-point of platinum, as may be shown by the apparatus represented in fig. 9.

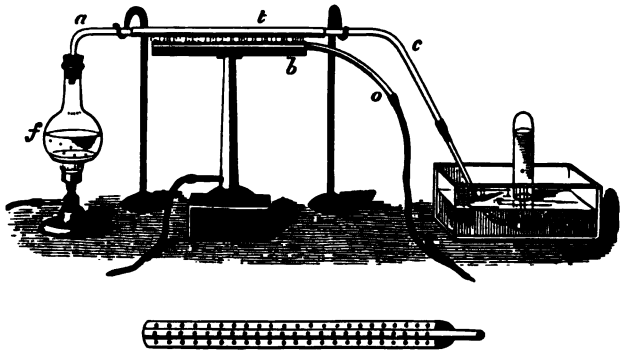


Fig. 9.—Decomposition of steam by heat.

A platinum tube (*t*) is heated by the burner *b*, the construction of which is shown at the bottom of the cut. It consists of a wide brass tube, from which the coal-gas issues through two rows of holes, between which oxygen is supplied through the holes in the narrow tube, brazed into a longitudinal slit between the two rows of holes in the gas tube. The oxygen is supplied from a gas bag or gas-holder, with which the pipe (*o*) is connected.

The flask (*f*) containing boiling water is furnished with a perforated cork, carrying a brass tube (*a*), which slips into one end of the platinum tube, into the other end of which another brass tube (*c*) is slipped; this is prolonged by a glass tube attached by india-rubber so as to deliver the gas under a small jar standing upon a bee-hive shelf in a trough.

The platinum tube is not heated until the whole apparatus is full of steam, and no more bubbles of air are seen to rise through the water in the trough; the gas burner is then lighted, and the oxygen turned on until the platinum tube is heated to a very bright red heat; bubbles of the mixture of hydrogen and oxygen produced by the decomposition of the water may then be collected in the small jar, and afterwards exploded by applying a flame.

In these experiments, the high temperature to which the steam is exposed causes its molecules to vibrate with such high velocities that the equilibrium of chemical attraction between their component atoms is disturbed, and new molecules of hydrogen and oxygen are produced. These are immediately carried out of the heated region by the current of steam.

* The end of the tube B should be bent upwards and thrust into a perforated cork with notches cut down the sides. By slipping this cork into the neck of the test-tube, the latter will be held firmly.

† With a powerful coil, a cubic inch of explosive gas may be collected in about fifteen minutes.

6. In this case, the force of chemical attraction holding the atoms of oxygen and hydrogen together in the form of water, has been overcome by the physical force of heat. But water may be more easily decomposed by acting upon it with some element which has sufficient chemical energy to enable it to displace the hydrogen.

No non-metallic element is capable of effecting this at the ordinary temperature. Among the practically important metals, there are five which have so powerful an attraction for oxygen that it is necessary to preserve them in bottles filled with some liquid free from that element, such as petroleum (composed of carbon and hydrogen), to prevent them from combining with the oxygen of the atmosphere. These metals are capable of decomposing water with great facility.

Metals which decompose water at the ordinary temperature.—Potassium, Sodium, Barium, Strontium, Calcium.

7. When a piece of potassium is thrown upon water, it takes fire and burns with a fine violet flame, floating about as a melted globule upon the surface of the water, and producing in the act of combination enough heat to kindle the hydrogen as it escapes. The violet colour of the flame is due to the presence of a little potassium in the form of vapour. The same results ensue if the potassium be placed on ice. The water in which the potassium has been dissolved is soapy to the touch and taste, and has a remarkable action upon certain colouring matters. Paper coloured with the yellow dye *turmeric* becomes brown when dipped in it, and paper coloured with *red litmus* becomes blue. Substances possessing these properties have been known from a very remote period as *alkaline* substances, apparently because they were first observed by the alchemists in the ashes of plants called *kali*. The alkalies are amongst the most useful of chemical agents.

8. *Definition of an alkali.*—A compound substance, very soluble in water, turning red litmus blue and turmeric brown.

These alkaline properties are directly opposed to the characters of sour or *acid** substances, such as vinegar or vitriol, which change the blue litmus to red. When an acid liquid, such as vinegar (acetic acid) or vitriol (sulphuric acid) is added to an alkaline liquid, the characteristic properties of the latter are destroyed, the alkali being *neutralised*.

An acid substance may be known by its property of neutralising an alkali (either entirely or partly).

The minute investigation into the action of potassium upon the water would require considerable manipulative skill. It would be necessary to weigh accurately the potassium employed, to evaporate the resulting solution in a silver basin (most other materials being corroded by the alkali), and after all the water had been expelled by heat, to ascertain the composition of the residue by a chemical analysis.

It would be found to contain by weight 1 part of hydrogen, 16 parts of oxygen, and 39 parts of potassium.

Since water contains 2 parts by weight of hydrogen, combined with 16 parts by weight of oxygen, it is evident that the product of the action of potassium on water is formed by the substitution of 39 parts of potassium for 1 part of hydrogen.

It is found that whenever potassium takes the place of hydrogen in a

* From ἀκή, a point, referring to the pungency or sharpness of the acid taste.

compound, 39 parts of the former are exchanged for one of the latter, and this is generally expressed by stating that 39 is the *chemical equivalent* of potassium.

The *chemical equivalent of a metal* expresses the weight of it which is required to be substituted for one part by weight of hydrogen in compounds of hydrogen.

9. The action of potassium upon water is an example of the production of compounds by substitution of one element for another, a mode of formation which is far more common than the production of compounds by direct combination of their elements.

If the symbol K represent 39 parts by weight of potassium, its action upon water would be represented by the chemical equation.

$$H_2O + K = KOH + H.$$
Water. Caustic potash.*

But since the atoms cannot exist, except in combination as molecules, it would be strictly correct to write the equation thus:

$$2H_2O + K_2 = 2KOH + H_2.$$

Since the molecular equation can always be obtained by doubling the atomic equation, the latter will be most commonly given in this work, as involving fewer numbers.

Sodium has a less powerful attraction, or affinity, for oxygen than potassium has; it does not, therefore, evolve so much heat when it combines with oxygen, for it is generally noticed that the greater the affinity between two elements the greater is the quantity of heat evolved when they combine. Thus sodium does not usually take fire when thrown upon cold water, although sufficient heat is evolved to fuse at once the metal. By holding a lighted match over the globule as it swims upon the water, the hydrogen may be kindled, when its flame is bright yellow, from the presence of the sodium. The solution is strongly alkaline from the *soda* produced.

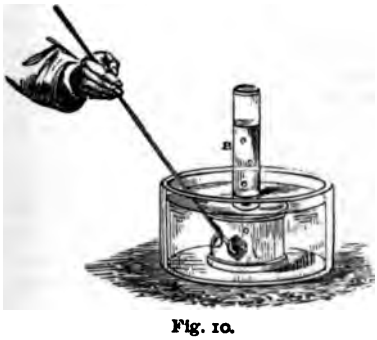


Fig. 10.

By placing the sodium on a piece of blotting-paper laid on the water, it may be made to ignite the hydrogen spontaneously, because the paper keeps the sodium stationary, and prevents it from being so rapidly cooled by the water. Several cubic inches of hydrogen may easily be collected by placing a piece of sodium as large as a pea in a small wire-gauze box (A, Fig. 10), and holding it under an inverted cylinder (B) filled with water and standing on a bee-hive shelf.†

The product of the action of sodium upon water contains 1 part by weight of hydrogen, 16 of oxygen, and 23 of sodium, so that the 23 parts of sodium have been exchanged for, or been found chemically equivalent to, 1 part of hydrogen.

* Caustic, from καίω, to burn, in allusion to its corrosive properties; and potash, from its having been originally prepared from the washings of wood ashes boiled down in iron pots and decomposed by lime.

† This experiment sometimes ends in an explosion.

Taking the symbol Na to represent 23 parts by weight of sodium, its action would be expressed thus: $H_2O + Na = NaOH + H$.

Barium, strontium, and calcium decompose water less rapidly than potassium and sodium do.

10. The increase in molecular motion caused by heat disturbs the equilibrium of chemical attraction, so that metals which refuse to decompose water at the ordinary temperature will do so if the temperature be raised, and accordingly magnesium and manganese, which are without action upon cold water, decompose it *at the boiling-point*, disengaging hydrogen, and producing magnesia (MgO, a feebly alkaline earth) and oxide of manganese (MnO).

But the greater number of the common metals must be raised to a much higher temperature than this before they will decompose water. The following metals abstract the oxygen from water at high temperatures, those at the commencement of the list requiring to be heated to redness (about 600° C.), and the temperature required progressively increasing until it attains whiteness for those at the end of the list.

Metals which decompose water at a temperature above a red heat.—Zinc, Iron, Chromium, Cobalt, Nickel, Tin, Antimony, Aluminium, Lead, Bismuth, Copper.

The *noble metals*, as they are called, which exhibit no tendency to oxidise in air, are incapable of removing the oxygen from water, even at high temperatures.

Metals which are incapable of decomposing water.—Mercury, Silver, Gold, Platinum.

Metals decompose water more readily when in a very fine state of division or placed in a state of electrical polarisation by contact with other metals more electro-negative than themselves. Thus zinc, in contact with precipitated copper, decomposes water slowly at the ordinary temperature, hydrogen being evolved, and zinc hydrate separated in white flakes.

The *copper-zinc couple* made by precipitating copper sulphate with zinc-foil in excess, and washing, is very useful in many operations where a slow production of hydrogen is required.

HYDROGEN.

H = 1 part by weight = 1 volume.

11. *Preparation of hydrogen.*—The simplest process, chemically speaking, for preparing hydrogen in quantity, consists in passing steam over red-hot iron. An iron tube (A, Fig. 11) is filled with iron nails and

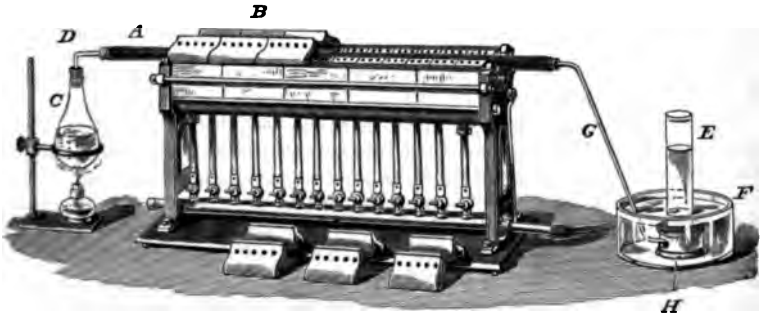


Fig. 11.—Preparation of hydrogen from steam.

placed in a furnace (B), where it is heated to redness by gas burners. A current of steam is then passed through it by boiling the water in the flask (C), which is connected with the iron tube by a glass tube (D) and perforated corks. The hydrogen is collected from the glass tube (G) in cylinders (E) filled with water, and inverted in the trough (F) upon the bee-hive shelf (H), the first portions being allowed to escape, as containing the air in the apparatus.

The iron combines with the oxygen of the water to form the black oxide of iron (Fe_3O_4) which will be found in a crystalline state upon the surface of the metal. The decomposition is represented by the equation $4H_2O + Fe_3 = Fe_3O_4 + H_8$.

The atomic weight of iron being 56, the Fe_3 in the above equation represent 56×3, or 168 parts by weight of iron.

Other methods for depriving steam of its oxygen, and therefore for preparing hydrogen, will be noticed in the sequel.

The process by which hydrogen is most commonly prepared consists in dissolving iron or zinc in a mixture of sulphuric acid and water.

Zinc is the most convenient metal for this purpose. It is used either in small fragments or cuttings, or as *granulated zinc*, prepared by melting it in a ladle and pouring it from a height of three or four feet into a pailful of water; when thus granulated it exposes a larger surface to the action of the acid. The zinc is placed in the bottle (A, Fig. 12), covered with water to the depth of two or three inches, and diluted sulphuric acid slowly poured in through the funnel tube (B) until a pretty brisk effervescence is observed. The hydrogen is unable to escape through the funnel tube, since the end of this is beneath the surface of the water, but it passes off through the bent tube (C), and is collected over water as usual, the first portion being rejected as containing air.

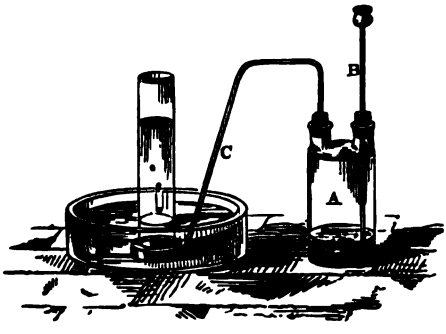


Fig. 12.—Preparation of hydrogen.

By allowing the solution left in the bottle to cool in another vessel, crystals of zinc sulphate (*white vitriol*) may be obtained.

It will be noticed that the liquid becomes very hot during the action of the acid upon the zinc, the heat being produced by the chemical combination. The black flakes which separate during the dissolution of the zinc are metallic lead, which is always present in the zinc of commerce, and much accelerates the evolution of hydrogen by causing galvanic action. Pure zinc placed in contact with diluted sulphuric acid evolves hydrogen very slowly. By attaching a piece of platinum to the pure zinc, so as to form a galvanic couple, the reaction may be considerably hastened.

The preparation of hydrogen by dissolving zinc in diluted sulphuric acid may be represented by the equation*

$$\underset{\text{Sulphuric acid.}}{H_2SO_4} + Zn = \underset{\text{Zinc sulphate.}}{ZnSO_4} + H_2.$$

The symbol Zn here represents an atom of zinc, which is 65 times as heavy as the atom of hydrogen. An atom of zinc has here displaced 2 atoms of hydrogen, whereas it was found that an atom of potassium displaced only 1 atom of hydrogen; this is often expressed by saying that potassium is a *monovalent* element—*i.e.* is exchangeable for 1 atom of hydrogen. But since 65 parts of zinc displace 2 parts of hydrogen, zinc is a *divalent* element—*i.e.* is exchangeable for 2 atoms of hydrogen. This is commonly expressed by writing the symbol of zinc Zn".

It may be supposed that the atom of a monovalent element, such as hydrogen or potassium, exerts its chemical attraction in one direction only, as represented by a single line or *bond* attached to the symbol, thus H–, K–; whilst a divalent element, such as zinc, exerts chemical attraction in two directions, represented by attaching two lines to the symbol, thus –Zn–, or Zn<. Since an atom of oxygen combines with two atoms of hydrogen, it must also exert chemical attraction in two directions, so that a molecule of water may be represented as H––O––H. The displacement of half the hydrogen by potassium (p. 17) then produces K––O––H, caustic potash, and the displacement of both atoms of hydrogen by zinc produces Zn< >O, or zinc and oxygen united by both their *bonds* of chemical attraction, forming zinc oxide.

Iron might be used instead of zinc, and the solution, when evaporated, would then deposit crystals of *green vitriol* or *copperas* (sulphate of iron, or ferrous sulphate, $FeSO_4$), the action of iron upon the sulphuric acid being represented by the equation $H_2SO_4 + Fe = FeSO_4 + H_2$, which shows that 1 atom (56) of iron has taken the place of 2 atoms of hydrogen, and that the iron is divalent, like zinc.

12. *Physical properties of hydrogen.*—This gas is invisible, and inodorous when pure. The hydrogen obtained by the ordinary methods has a very disagreeable smell, caused by the presence of minute quantities of compounds of hydrogen with sulphur, arsenic, and carbon; but the gas prepared with pure zinc and sulphuric acid is quite free from smell. The most remarkable physical property of hydrogen is its lightness. It is the lightest of all kinds of matter, being about $\frac{1}{15}$ as heavy as air, and $\frac{1}{11246}$ as heavy as water.

The lightness of hydrogen may be demonstrated by many interesting experiments. Soap bubbles or small balloons (of *collodion*, for example) will ascend very rapidly if inflated with hydrogen. A light beaker glass may be accurately weighed in a pair of scales; it may then be held with its mouth downwards, and the hydrogen poured up into it from another vessel. If it be then replaced upon the scale-pan with its mouth downwards, it will be found very much lighter than before. Another form of the experiment is represented in Fig. 13, where a light glass shade has been suspended from the balance and counterpoised, the equilibrium being, of course, at once disturbed when hydrogen is poured up into the shade. If a stoppered gas jar full of hydrogen be held with its mouth downwards, and a piece of smouldering brown paper held under it, the smoke, which would rise freely in the air, is quite unable to rise through the hydrogen, and remains at the mouth of the jar until the stopper is removed, when the hydrogen quickly rises and the smoke follows it.

* In this equation the excess of water which must be added to dissolve the zinc sulphate is not set down. Hydrogen could not be prepared according to the equation as it stands, because the zinc sulphate would collect round the metal and prevent further action.

13. The employment of hydrogen for filling balloons renders a knowledge of the relation between the weights of equal volumes of hydrogen and atmospheric air of great importance. The number expressing this relation is termed the *Specific Gravity* of hydrogen.

(DEFINITION.—The specific gravity of a gas or vapour is the weight of a volume of it compared with that of an equal volume of some other gas, selected as a standard, at the same temperature and pressure.)

If the weight of a given volume of purified and dried air be represented as unity, an equal volume of hydrogen, at the same temperature and pressure, would weigh 0.0695, which is expressed by saying that the specific gravity of hydrogen (air = 1) is 0.0695.

Fig. 13.

In ascertaining the weights of different volumes of gases, it is of the greatest importance that they should have some definite temperature and pressure, since the volume of a given weight of gas is augmented by increase of temperature and by decrease in pressure. It is usual to state the weights of gases, either at 60° Fahrenheit and 30 inches barometer, or at 0° Centigrade and 760 millimetres barometer.

One litre of hydrogen at 0° C. and 760 mm. Bar. weighs 0.09 gram, so that one gram (15.43 grains) of hydrogen, at 0° C. and 760 mm. Bar., measures 11.11 litres (one litre = 61.024 cubic inches = 1.76 pint).

One grain of hydrogen, at 60° F. and 30 inches Bar., measures 46.45 cubic inches.

It is now easy to calculate how much zinc it would be necessary to dissolve in sulphuric acid in order to obtain any desired volume, say 100 litres, of hydrogen. Referring to the equation for the preparation of hydrogen, $Zn + H_2SO_4 = H_2 + ZnSO_4$, and remembering that Zn represents 65 parts by weight of zinc, and H_2 represent 2 parts by weight of hydrogen, such a problem can be solved by ordinary proportion; thus—

(2 grams H) 22.22 litres : 100 litres : : 65 grams zinc : x.

$x = 292$ grams zinc give 100 litres of hydrogen at 0° C. and 760 mm. Bar.

14. It will be observed, in the experiment with the balance (Fig. 13), that the gas gradually *falls* out of the jar, notwithstanding its lightness, and is displaced by air; so that, after a time, the equilibrium is restored, proving that the molecules of hydrogen possess motion which is independent of gravitation. This motion of the molecule gives rise to the phenomenon known as *diffusion*.

Diffusion is the intermixture of molecules brought about by their power of moving amongst each other. This power is possessed in the highest degree by gaseous molecules, all gases being capable of perfect and comparatively rapid intermixture. Some liquids, such as alcohol and water, also intermix perfectly, although comparatively slowly, whilst other liquids, such as oil and water, diffuse into each other only to a very limited extent. When alcohol is poured on to water, it forms a separate layer on the surface of the water, because it is the specifically lighter of the two; after a time, however, the two layers are no longer discernible, and the liquid is a homogeneous mixture of alcohol and water. In the same way hydrogen will float on air, but only for a very short time, since the *rate of diffusion* of this gas is very rapid. A homogeneous mixture of hydrogen and air is speedily formed.

Even among solids the phenomenon of diffusion is not unknown; thus a piece of gold lying on a piece of lead will gradually diffuse through the lead, but the process occupies years.

The molecules of all gases do not move with the same velocity, so that some gases diffuse more rapidly than others. This has been discovered by confining a gas in a vessel closed by some material having very minute pores, and immersing the vessel in an atmosphere of some other gas. The passage of the molecules through the pores of the material closing the vessel is sufficiently slow to allow of a comparison between the velocities of passage or *rates of diffusion* of the two gases.

The *diffusion tube* (Fig. 14) employed for this purpose is a glass tube (A) closed at one end by a plate of plaster of Paris (B). If this tube be filled with hydrogen,* and its open end immersed in coloured water, the water will be observed to rise rapidly in the tube, on account of the rapid escape of the hydrogen through the pores of the plaster. The external air, of course, passes into the tube through the pores at the same time, but much less rapidly than the hydrogen passes out, so that the ascent of the column of water (C) marks the difference between the volume of hydrogen which passes out, and that of air which passes into the tube in a given time, and allows a measurement to be made of the *rate of diffusion;* that is, of the velocity with which the gas issues as compared with the velocity with which the air enters, this velocity being always taken as unity.† To determine the rate of diffusion, it is of course necessary to maintain the water at the same level within and without the diffusion tube, so as to exclude the influence of pressure.

This method has disclosed the *law of diffusion of gases*, namely, that

* This tube must be filled by displacement (see Fig. 20), in order not to wet the plaster. A piece of sheet caoutchouc may be tied over the plaster of Paris, so that diffusion may not commence until the sheet is removed.

† Air being a mixture of nitrogen and oxygen, its rate of diffusion is intermediate between the rates of those gases; however, since the proportions of the gases are very nearly constant, no error of any magnitude arises.

the *rates of diffusion of gases vary inversely as the square roots of their relative weights.* Thus, oxygen is 16 times as heavy as hydrogen, so that the rate of diffusion of hydrogen : the rate of diffusion of oxygen : : $\sqrt{16} : \sqrt{1}$; in other words, hydrogen will mix with another gas four times as fast as oxygen will mix with that gas.

To prove that the ascent of the hydrogen due to its lightness is not instrumental in drawing up the water in the diffusion tube, the experiment may be made as in

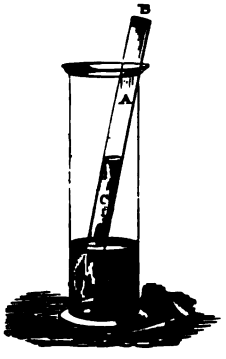


Fig. 14.—Diffusion tube.

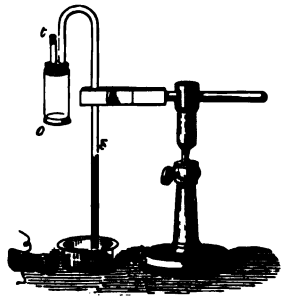


Fig. 15.

Fig. 15, where the plate of plaster (*o*) is turned downwards, so that the diffusion is made to take place in opposition to the action of gravity. This tube is filled by passing hydrogen in through the tube (*s*), and allowing the air to escape through (*t*), which is afterwards closed by a cork. The plaster of Paris (*o*) is tied over with caoutchouc whilst the tube is filled.

Since the relation between the weights of equal volumes of hydrogen and air is that of 0.069 : 1, the rates of diffusion are as 1 : $\sqrt{0.069}$—that is, hydrogen diffuses about 3.8 times as rapidly as atmospheric air, or 3.8 measures of hydrogen will pass out of the diffusion tube whilst one measure of air is passing in. In a similar manner hydrogen would escape through minute openings with four times the velocity of oxygen ; and laboratory experience shows that a cracked jar, or a bottle with a badly fitting stopper, may often be used to retain oxygen but not hydrogen.

A very striking illustration of the high rate of diffusion of hydrogen is arranged as represented in Fig. 16. A is a cylinder of porous earthenware (such as are employed in galvanic batteries) closed at one end, and furnished at the other with a perforated caoutchouc stopper or a cork bung, through which passes a glass tube B, about six feet long and half an inch in diameter. The bung is made air-tight by coating it with sealing-wax dissolved in spirit of wine. This tube being supported so that its lower end dips about an inch below the surface of water, a jar of coal-gas is held over the porous cylinder, when the velocity of the particles of the gas is manifested by their being forced (not only out of the mouth of the jar C, which is open at the bottom, but also) through the pores of the earthenware jar, the air from which is violently driven out, as if by blowing, through the tube, and is seen bubbling up rapidly through the water. When the air has ceased to bubble out, and a large volume of gas has entered the porous jar, the bell-jar C is removed, when the gas escapes so rapidly through the pores, that a column of twenty to thirty inches of water is drawn rapidly up the tube B. If the greatest height to which the water ascends be marked, and when it has returned to its former level, a jar of hydrogen be held over the porous cylinder, it will be found that the above phenomena are manifested in a much higher degree, showing that coal-gas, being heavier than hydrogen, does not pass nearly so rapidly through the pores of the earthenware as hydrogen does.

By connecting the porous cylinder A, by means of a short piece of tube, with a two-necked bottle, like that represented in Fig. 20, and passing through a cork in the other neck, a piece of tube extending to the bottom of the bottle and drawn out

to an open point at its upper extremity, water may be forced out in a stream of two or three feet in height by holding the jar of hydrogen over the porous cylinder.

The great difference in the rates of diffusion of hydrogen and oxygen may be easily shown by the arrangement represented in Fig. 17. *A* is a jar filled with a mixture of two volumes of oxygen with one volume of hydrogen, communicating through the stop-cock and flexible tube with the glass tube *B*, which is fitted through a perforated cork in the bowl of the common tobacco-pipe *C*, the sealing-waxed end of which dips under water in the trough *D*. By opening the stop-cock and pressing the jar down in the water, the mixed gases may be forced rapidly through the pipe, and if a small cylinder (*E*) be filled with them, the mixture will be found to detonate violently on the approach of a flame. But if the gas be made to pass very slowly through the pipe (at the rate of about a cubic inch per minute), the hydrogen will diffuse through the pores of the pipe so much faster than the oxygen, that the gas collected in the cylinder will contain so little hydrogen as to be no longer explosive, and to exhibit the property of oxygen to rekindle a partly extinguished match.

Fig. 16.

The fact that the phenomenon of diffusion is shown by solids and liquids as well as by gases has led to the conclusion that in all three states of matter the molecules are in constant motion. In a solid the distance through which each molecule moves is very small because the molecules are so close together that they attract and hinder each other. It is supposed that heat increases the motion until presently the molecules are moving rapidly enough partly to counteract their attraction for each other, whereupon the solid melts to a liquid. In the liquid the molecules are still under the influence of each other so that they cannot move freely through space, which is the characteristic of gaseous molecules. By heating the liquid it eventually boils and becomes a vapour, which, when its temperature is considerably above that at which the liquid boils, has the properties of a gas.

In a true gas the molecules would move without influencing each other in any regard, except in so far as they might collide and rebound like billiard-balls. They would never stick together, so to speak.

Now it has been shown by experiment that *the volume of a gas varies inversely as the pressure to which it is subjected* (Boyle's Law). Thus, if 1000 c.c. of hydrogen be measured when the barometer stands at 760 mm., this volume will become 500 c.c. when the pressure is increased to $760 \times 2 = 1520$ mm., or 2000 c.c. when the pressure is diminished to 380 mm.

It has further been shown that *the volume of a gas is directly*

proportional to its absolute temperature, that is, the temperature shown by the Centigrade thermometer + 273 (Charles' Law). For example, 1000 c.c. of hydrogen at 273° abs. become 2000 c.c. at 546° abs. or 500 c.c. at 136.5° abs.

But although these laws have been experimentally discovered, it is acknowledged that no known gas conforms with them absolutely, and particularly do gases deviate from them when under high pressure or at low temperature. This is because under these conditions the gases are nearer the liquid condition than they are under low pressure or at high temperature; the molecules are nearer together and more under the influence of each other.

It has been proved by mathematics that the ideal gas would obey the

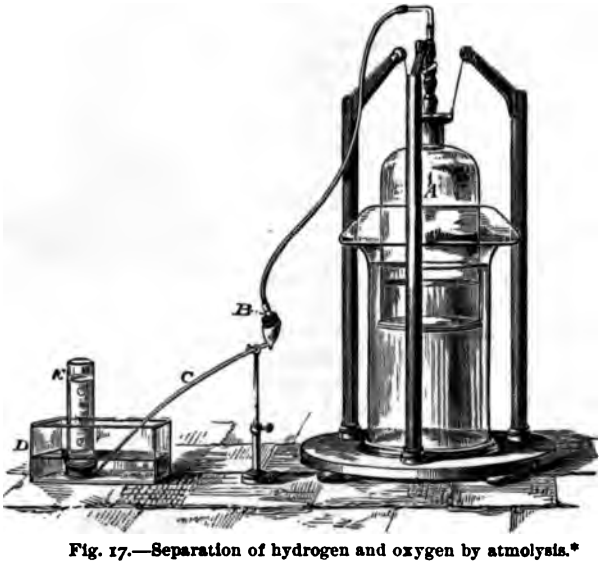


Fig. 17.—Separation of hydrogen and oxygen by atmolysis.*

laws of Boyle and Charles accurately, and different gases certainly differ in the degree to which they deviate from the laws, so that degrees of gaseous state, or good and bad gases, may be recognised. Those gases deviate least which are the most difficult to liquefy, for they are farthest removed from the liquid state. Hydrogen is the best gas, in this sense, that is known, hence on this account, as well as on account of its lightness, it is the best standard for comparison of weights and volumes of gases. Carbon dioxide, on the other hand, is a poor gas at the ordinary temperature and pressure, for it is then not far above its liquefying point; but it improves if its temperature is raised or its pressure reduced.

The diminution which occurs in the volume of a gas when the pressure upon it is increased, or when the temperature of it is decreased, can only be ascribed to the approachment of the molecules nearer to each other. When the distance between the molecules is

* This term has been applied to the separation of gases by diffusion; ἀτμός, *vapour*; λύω, to loosen.

sufficiently diminished the gas becomes a liquid. Thus it is that all gases can be liquefied by great pressure or extreme cold, or a combination of the two. Hydrogen has been proved to be the most difficult of common gases to liquefy, but this object has at length been achieved, and liquid hydrogen is found to be transparent, colourless, and mobile; it boils at -252° C. and freezes to colourless crystals at -257° C.

There is a temperature for every gas above which no amount of pressure can liquefy the gas; this is called the *critical temperature* of that gas, or the *absolute boiling-point* of the corresponding liquid.

This value for hydrogen appears to be -242° C., but for some gases, such as carbon dioxide, it is above the ordinary temperature, so that they can be liquefied by pressure alone. The pressure required to liquefy a gas at its critical temperature is called the *critical pressure* of the gas, that of hydrogen being 15 atmospheres. The liquefaction of gases is further treated of under *Air*.

Fig. 18.

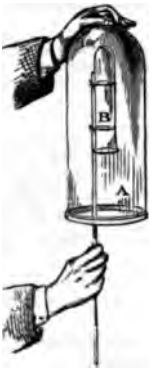


Fig. 19.

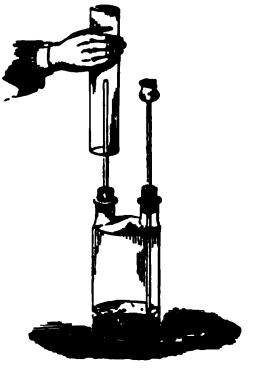


Fig. 20.

Hydrogen is one of the least soluble of gases; 100 volumes of water dissolve only 1.83 vols. of the gas at 15° C. This is only to be expected from the difficulty with which it is liquefied, it being generally the case that the more easily liquefied gases are the more soluble.

15. *Chemical properties of hydrogen.*—The most conspicuous chemical property of hydrogen is its disposition to burn in air when raised to a moderately high temperature, entering into combination with the oxygen of the air to form water. The formation of water during the combustion of hydrogen gave rise to its name (*ὕδωρ*, water).

Since an *atom* of oxygen combines with two *atoms* of hydrogen to form water, the gases will not combine unless under the influence of some force, such as heat or electricity, to assist in resolving their *molecules* into the constituent atoms.

On introducing a taper into an inverted jar of hydrogen (Fig. 18), the flame of the taper is extinguished, but the hydrogen burns with a pale flame at the mouth of the jar, and the taper may be rekindled at this flame by slowly withdrawing it.

The lightness and combustibility of hydrogen may be illustrated simultaneously by some interesting experiments. If two equal gas cylinders be filled with hydrogen, and held with their mouths respectively upwards and downwards, it will be found on testing each with a taper after the same interval, that the

hydrogen has entirely escaped from the cylinder held with its mouth upwards, whilst the other still remains nearly filled with the gas.

The hydrogen may be scooped out of the jar A (Fig. 19) with the small cylinder B attached to a handle. On removing B, and applying a taper to it, the gas will take fire.

A cylinder may be filled with hydrogen by displacement of air (Fig. 20), if the tube from the hydrogen bottle be passed up into it.

If such a dry cylinder of hydrogen be kindled whilst held with its mouth downwards, the formation of water during the combustion of the hydrogen will be indicated by the deposition of dew upon the sides of the cylinder.

By softening a piece of glass tube in the flame of a spirit-lamp, drawing it out and filing it across in the narrowest part (Fig. 21), a jet can be made from which the hydrogen may be burnt. This jet may be fitted by a perforated cork to any common bottle for containing the zinc and sulphuric acid (Fig. 22).

The hydrogen must be allowed to escape for some minutes before applying a light, because it forms an explosive mixture with the air contained in the bottle.

Fig. 21.

Fig. 22.

This may be proved, without risk, by placing a little granulated zinc in a soda-water bottle (old form), pouring upon it some diluted sulphuric acid, and quickly inserting a perforated cork, carrying a piece of glass tube about three inches long, and one-eighth of an inch wide. If this tube be immediately applied to a flame, the mixture of air and hydrogen will explode, and the cork and tube will be projected to a considerable distance.

By inverting a small test-tube over the jet in Fig. 22, a specimen of the hydrogen may be collected, and may be kindled, to see if it burns quietly, before lighting the jet.

A dry glass, held over the flame, will collect a considerable quantity of water, formed by the combustion of the hydrogen.

The combustion of hydrogen produces a greater heating effect than that of an equal weight of any other combustible body. It has been determined that 1 gram of hydrogen, in the act of combining with 8 grams of oxygen, produces enough heat to raise 34,462 grams of water from 0° C. to 1° C. The temperature of the hydrogen flame is probably about 2000° C. Notwithstanding its high temperature, the flame of hydrogen is almost devoid of illuminating power, on account of the absence of solid particles.

16. If a taper be held several inches above a cylinder of hydrogen, standing with its mouth upwards, the gas will be kindled with a loud explosion, because an explosive mixture of hydrogen and air is formed in and around the mouth of the cylinder.

A stoppered glass jar (Fig. 23) is filled with hydrogen and supported upon three blocks; if the hydrogen be kindled at the neck of the jar, it will burn quietly until air has entered from below in sufficient proportion to form an explosive mixture, which will then explode with a loud report.

The same experiment may be tried on a smaller scale, with the two-necked copper vessel (Fig. 24), the lower aperture being opened some few seconds after the hydrogen has been kindled at the upper one.

The explosion of the mixture of hydrogen and air is due to the sudden expansion caused by the heat generated in the combination of the

hydrogen with the oxygen throughout the mixture. After the explosion of the mixture of hydrogen and air (oxygen and nitrogen), the substances present are steam (from the combination of the hydrogen and oxygen) and nitrogen, which are expanded by the heat developed in the combination, to a volume far greater than the vessel can contain,

Fig. 23.

Fig. 24.

so that a portion of the gas and vapour issues very suddenly into the surrounding air, the collision with which produces the report.

If pure oxygen be substituted for air, the explosion will be more violent, because the mixture is not diluted with the inactive nitrogen. The further study of this subject must be preceded by that of oxygen.

OXYGEN.

O = 16 parts by weight = 1 volume.

17. Oxygen is the most abundant of the elementary substances. It constitutes about one-fifth (by volume) of atmospheric air, where it is merely *mixed*, not combined, with the nitrogen, which composes the bulk of the remainder. Water contains eight-ninths (by weight) of oxygen; whilst silica and alumina, which compose the greater part of the solid earth (as far as we know it), contain about half their weight of oxygen.

Before inquiring which of these sources will most conveniently furnish pure oxygen, it will be desirable for the student to acquire some knowledge of the properties of this element, and of the chemical relations which it bears to other elementary bodies, for without such knowledge it will be found very difficult to understand the processes by which oxygen is procured.

18. *Physical properties of oxygen.*—From the fact that it occurs in an uncombined state in the atmosphere, it will be inferred that oxygen is perfectly invisible, and without odour. It is a little more than one-tenth heavier than air, which is expressed in the statement that its specific gravity is 1.105.

In the study of theoretical chemistry, it is expedient to select hydrogen instead of air as the standard with which the specific gravities of

gases are compared; for the atomic weights are also referred to hydrogen as the unit, and in the case of the common elementary gases the *atomic weights are identical with their specific gravities* (H = 1). Thus the specific gravity of oxygen (H = 1) is 16, or, more exactly, 15.88. It will be found convenient to remember that *the specific gravity of a gas or vapour is the weight in grams of* 11.11 *litres of it.*

Oxygen boils at − 182° C. under atmospheric pressure, so that it is liquid at temperatures below this.

The liquid has a steel-blue colour; its sp. gr. at − 182° C. is 1.135 (water = 1); its critical temperature (p. 25) is − 119° C., and its critical pressure is 51 atmospheres. The liquid is attracted by a magnet. Owing to its low temperature liquid oxygen is chemically very inactive, and has no action on such readily oxidisable substances as phosphorus, sodium or potassium. A mixture of powdered charcoal and liquid oxygen can, however, be detonated by exploding a small charge of mercuric fulminate in it.

Oxygen is slightly soluble in water; 100 volumes of water absorb 4 volumes of oxygen at 0° C. and 3 volumes at 15° C.

19. *Chemical properties of oxygen.*—This element is remarkable for the wide range of its chemical attraction for other elementary bodies, with all of which, except two, it is capable of entering into combination. *Fluorine and bromine are the only elements which are not known to unite with oxygen.**

With nearly all the elements oxygen combines in a direct manner; that is, without the apparent intervention of any third substance, although, since it has been proved that *perfectly dry* oxygen will not combine with other elements, it must be admitted that moisture (or some other third substance) is essential to the chemical combination.†

There are only *seven elements* (among those of practical importance) *which do not unite in a direct manner with oxygen*—viz. *chlorine, bromine, iodine, fluorine, gold, silver, platinum.*

(Definition.—The compounds of oxygen with other elements are called *Oxides.*)

The act of combination with oxygen, or *oxidation*, is generally a slow process, and its effects are not immediately perceived. Some familiar examples of oxidation are—the tarnishing or rusting of metals by air, the gradual decay of wood, the *drying* of oils in paint, the formation of vinegar from alcoholic liquids, the respiration of animals and combustion.

In all these processes heat is generated; but it is not usually noticed unless it is sufficient to render the particles of matter luminous, which is the case only with combustion.

(Definition.—*Combustion* is chemical combination attended with heat and light.)

20. *Phosphorus, the only non-metal which combines with oxygen at the ordinary temperature*, affords a good illustration of oxidation. This element, a solid at the ordinary temperature, is preserved in bottles filled with water, on account of the readiness with which the oxygen of the air combines with it. If a small piece of phosphorus be dried by

* The newly discovered elements argon, helium, krypton, neon and xenon, do not combine with oxygen.

† Charcoal may be heated to redness in *dry* oxygen without visible combustion. Sulphur and phosphorus, which inflame in moist oxygen at 260° C. and 60° C. respectively, may be distilled in the dry gas at 440° C. and 290° C. respectively.

gentle pressure between blotting-paper, and exposed to the air, its particles begin to combine at once with oxygen, and the heat thus developed slightly raises the temperature of the mass.

Now, *heat generally encourages chemical union*, so that the effect of this rise of temperature is to induce a more extensive combination of the phosphorus with the oxygen, causing a greater development of heat in a given time, until the temperature is sufficient to render the particles brilliantly luminous, and a true case of combustion results—the combination of the phosphorus with oxygen, attended with production of heat and light. In cold weather, the phosphorus seldom takes fire until rubbed, or touched with a hot wire.

(DEFINITION.—*Combustion in air* is the chemical combination of the elements of the combustible with the oxygen of the air, attended with development of heat and light.)

If a dry glass (Fig. 25) be placed over the burning phosphorus, the thick white smoke which proceeds from it may be collected in the form of snowy flakes. These flakes are commonly termed *phosphoric oxide* or *phosphoric anhydride*,* and are composed of 80 parts by weight of oxygen, and 62 parts of phosphorus (P_2O_5).

Fig. 25.

If the white flakes are exposed to the air for a short time, they attract moisture and become little drops, which have a very sour or *acid* taste. It was mentioned at page 19 that all substances which have such a taste have been found also to be capable of changing the blue colour of *litmus*† to red; whence the chemist is in the habit of employing paper dyed with blue litmus for the recognition of an acid.

(DEFINITION.—*Anhydride*, a compound which produces an acid when brought into contact with water.)

For the exact definition of an acid, see page 35.

During the slow combination of phosphorus with the oxygen of the air, before actual combustion commences, only 48 parts of oxygen unite with 62 parts of phosphorus, forming the substance called *phosphorous oxide* or *phosphorous anhydride* (P_2O_3).

(DEFINITION.—*The endings -ous and -ic* distinguish between two compounds formed by oxygen with the same element; *-ous* implying the smaller proportion of oxygen.)

Unless the temperature of the air be rather high, the fragment of phosphorus will not take fire spontaneously, but its combustion may always be ensured by exposing a larger surface to the action of the air. As a general rule, *a fine state of division favours chemical combination*, because the attractive force-inducing combination operates only between substances in actual contact; and the smaller the size of the particles, the more completely will this condition be fulfilled.

Thus if a small fragment of dry phosphorus be placed in a test-tube, and

* *Anhydride*, or without water, from ἀν, negative, and ὕδωρ, water.

† A colouring matter prepared from a lichen, *Roccella tinctoria*; the cause of the change of colour will be more easily understood hereafter.

dissolved in a little *carbon bisulphide*, the solution when poured upon blotting-paper (Fig. 26), will part with the solvent by evaporation, leaving the phosphorus in a very finely divided state upon the surface of the paper, where it is so rapidly attacked by the oxygen of the air that it bursts spontaneously into a blaze.

Though the light emitted by phosphorus burning in air is very brilliant, it is greatly increased when pure oxygen is employed; for since the nitrogen with which the oxygen in air is mixed takes no part in the act of combustion, it impedes and moderates the action of the

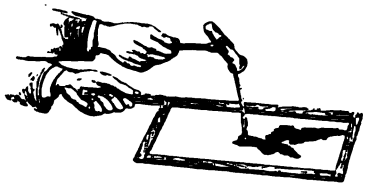


Fig. 26.

Fig. 27.—Phosphorus burning in oxygen.

oxygen. Each volume of the latter gas is mixed, in air, with four volumes of nitrogen, so that we may suppose five times as many particles of oxygen to come into contact, in a given time, with the particles of the phosphorus immersed in the pure gas, which will account for the great augmentation of the temperature and light of the burning mass.

To demonstrate the brilliant combustion of phosphorus in oxygen, a piece not larger than a good-sized pea is placed in a little copper or iron cup upon an iron stand (Fig. 27), and kindled by being touched with a hot wire. The globe (of thin well-annealed glass), having been previously filled with oxygen, and kept in a plate containing a little water, is placed over the burning phosphorus.

It will be observed that the same white clouds of phosphoric anhydride are formed, whether phosphorus is burnt in oxygen or in air, exemplifying the fact that *a substance will combine with the same proportion of oxygen whether its combustion be effected in pure oxygen or in atmospheric air*. The apparent increase of heat is due to the combustion of a greater weight of phosphorus in a given time and space. The total heating effect produced by the combustion of a given weight of phosphorus is the same whether air or pure oxygen be employed.

Fig. 28.—Sulphur burning in oxygen.

21. Sulphur (*brimstone*) affords an example of a non-metallic element which will not enter into combination with oxygen until its temperature has been raised very considerably. When sulphur is heated in air, it soon melts; and when its temperature reaches 500° F. (260° C.), it takes fire, burning with a pale blue flame. If the burning sulphur be plunged into a jar of oxygen, the blue light will become very brilliant, but the same act of combination occurs —32 parts by weight of oxygen uniting with 32 parts of sulphur to form

sulphurous acid gas or *sulphurous anhydride* (SO_2), which may be recognised in the jar by the well-known suffocating smell of brimstone matches. The experiment is most conveniently performed by heating the sulphur in a *deflagrating spoon* (A, Fig. 28), which is then plunged into the jar of oxygen, its collar (B) resting upon the neck of the jar, which stands in a plate containing a little water. The water absorbs a part of the sulphurous acid gas, and will be found capable of strongly reddening litmus-paper. It is possible to produce, though not by simple combustion, a compound of sulphur with half as much more oxygen (SO_3, sulphuric anhydride), showing that *a substance does not always take up its full share of oxygen when burnt.*

The luminosity of the flame of sulphur is far inferior to that of phosphorus, because, in the former case, there are no extremely dense particles in the flame corresponding with those of the phosphoric oxide produced in the combustion of phosphorus.

22. Carbon, also a non-metallic element, requires the application of a higher temperature than sulphur does to induce it to enter into direct union with oxygen; indeed, perfectly pure carbon appears to require a heat approaching whiteness to produce this effect. But charcoal (the carbon in which is associated with not inconsiderable proportions of hydrogen and oxygen) begins to burn in air at a much lower temperature; and if a piece of wood charcoal, with a single spot heated to redness, be lowered into a jar of oxygen, the adjacent particles will soon be raised to the combining temperature, and the whole mass will glow intensely, 32 parts by weight of oxygen uniting with 12 parts of carbon to form *carbonic acid gas* (CO_2) or *carbonic anhydride*, which will redden a piece of moistened blue litmus-paper suspended in the jar. It should be remembered that *carbon is an essential constituent of all ordinary fuel, and carbonic acid gas is always produced by its combustion.*

It will be noticed that the combustion of the charcoal is scarcely attended with flame; and when pure carbon (diamond, for example) is employed, no flame whatever is produced in its combustion, because carbon is not convertible into vapour, and all *flame is vapour or gas in the act of combustion;* hence, *only those substances burn with flame which are capable of yielding combustible gases or vapours.*

23. The three examples of sulphur, phosphorus and carbon sufficiently illustrate the tendency of non-metals to form acids by union with oxygen and water, which originally led to the adoption of its name, derived from ὀξύς, acid, and γεννάω, I produce. *All the common non-metallic elements, except hydrogen, bromine and fluorine, are capable of forming anhydrides, by their union with oxygen.*

Definition of an acid.—A compound containing hydrogen, which, when in contact with alkali (p. 19) exchanges its hydrogen, or a portion of it, for the alkali metal.

For example—

HCl	+	$NaOH$	=	$NaCl$	+	H_2O
Hydrochloric acid.		Soda.		Sodium chloride.		Water.
H_2SO_4	+	$2KOH$	=	K_2SO_4	+	$2H_2O$
Sulphuric acid.		Potash.		Potassium sulphate.		Water.
H_3PO_4	+	$2NaOH$	=	Na_2HPO_4	+	$2H_2O$
Phosphoric acid.		Soda.		Sodium phosphate.		Water.

24. The metals, as a class, exhibit a greater disposition to unite

directly with oxygen, though few of them will do so in their ordinary condition, and at the ordinary temperature. Several metals, such as iron and lead, are superficially oxidised when exposed to air under ordinary conditions, but this would not be the case unless the air contained water and carbonic acid gas, which favour the oxidation in a very decided manner. Among the metals which are of importance in practice, five only are oxidised by exposure to dry air at the ordinary temperature, viz., potassium, sodium, barium, strontium, and calcium, the attraction of these metals for oxygen being so powerful that they must be kept under petroleum, or some similar liquid free from oxygen. On the other hand, three of the common metals, silver, gold, and platinum, have so little attraction for oxygen that they cannot be induced to unite with it directly, even at high temperatures.

If a lump of sodium be cut across with a knife, the fresh surfaces will exhibit a splendid lustre, but will very speedily tarnish by combining with oxygen from the air, which gives rise to a coating of *sodium oxide*, and this to some extent protects the metal beneath from oxidation. The freshly cut sodium shines in the dark like phosphorus. Even when the attraction of the sodium for oxygen is increased by the application of heat, it is long before the mass of sodium is oxidised throughout, unless the temperature be sufficiently high to convert a portion of the sodium into vapour, which bursts through the crust of oxide, and burns with a yellow flame; if, when this has occurred, the spoon in which the sodium is heated (see Fig. 28) be plunged into a jar of oxygen, the yellow flame will be more brilliant.

Sixteen parts by weight of oxygen (1 atom) here combine with 46 parts of sodium (2 atoms) to form sodium oxide (Na_2O), which remains in the spoon in a fused state. When the spoon is cool, it may be placed in water, which will dissolve the oxide, converting it into the alkali soda,

$$\underset{}{Na_2O} + \underset{\text{Water.}}{H_2O} = \underset{\text{Soda.}}{2NaHO}$$

25. Zinc serves as an example of a metal which has no disposition to enter into combination with oxygen at the ordinary temperature,* but is induced to unite with it by a very moderate heat. If a little zinc (*spelter*) be melted in a ladle or crucible, and stirred about with an iron rod, it burns with a beautiful greenish flame, produced by the union of the vapour of zinc with the oxygen of the air. But the combustion is far more brilliant if a piece of zinc foil be made into a tassel, gently warmed at the end, dipped into a little flowers of sulphur, kindled, and let down into a jar of oxygen, when the flame of the burning sulphur will ignite the zinc, which burns with great brilliancy. On withdrawing what remains of the tassel after the combustion is over, it will be found to consist of a brittle mass, which has a fine yellow colour while hot, and becomes white as it cools. This is the *zinc oxide* (ZnO), formed by the union of 16 parts by weight of oxygen with 65 parts of zinc.

The zinc oxide does not possess the properties of an acid or an alkali, and belongs to another class of compounds termed *bases*, which are not soluble in water as the alkalies are, but, like them, are capable of neutralising the acids either partly or entirely. Thus, if the zinc oxide were added to diluted sulphuric acid as long as the acid would dissolve

* Unless water and carbonic acid gas be present, as in common air.

it, the well-known corrosive properties of the acid would be destroyed, although it would still retain the power of reddening blue litmus, and the solution would now contain a new substance, or *salt*, called *zinc sulphate* ($ZnSO_4$).

(DEFINITION.—A *base* is a compound body which is capable of neutralising an acid, either partly or entirely.)

It will be observed that an *alkali* is only a particular species of base, and might be defined as *a base which is very soluble in water*.

(DEFINITION.—A *salt* is a compound formed when the hydrogen in an acid is exchanged, either entirely or partly, for a metal; thus sodium chloride, NaCl, is formed by the exchange of the H in HCl, hydrochloric acid, for sodium; sodium phosphate, Na_2HPO_4, is formed from phosphoric acid, H_3PO_4, by the substitution of sodium for two-thirds of the hydrogen.)

26. Iron, in its ordinary form, like zinc, is not oxidised by *dry* air or oxygen at the ordinary temperature; but if it be heated even to only 500° F. a film of oxide of iron forms upon its surface, and as the temperature is raised, the thickness of the film increases, until eventually it becomes so thick that it can be detached by hammering the surface, as may be seen in a smith's forge. If an iron rod as thick as the little finger be heated to whiteness at the extremity, and held before the nozzle of a powerful bellows, it will burn brilliantly throwing off sparks and dropping melted oxide of iron. If a stream of oxygen be substituted for air, the combustion is of the most brilliant description A watch-spring (iron combined with about 1 per cent. of carbon) may be easily made to burn in oxygen by heating it in a flame till its elasticity is destroyed, and coiling it into a spiral (A, Fig. 29), one end of which is fixed, by means of a cork, in the deflagrating collar B; if the other end be filed thin and clean, dipped into a little sulphur, kindled and immersed in a jar of oxygen (C) standing in a plate of water, the burning sulphur will raise the temperature of the iron to the point of combustion, and the spring will be converted into molten drops of oxide.

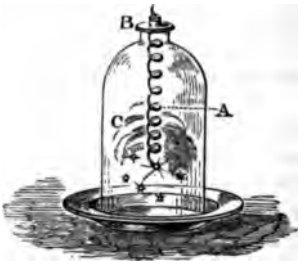


Fig. 29.—Watch-spring burning in oxygen.

The black oxide of iron formed in all these cases is really a combination of two distinct oxides of iron, one of which contains 16 parts by weight of oxygen and 56 parts of iron, and would be written FeO, whilst the other contains 48 parts of oxygen and 112 parts of iron, expressed by the formula Fe_2O_3. To distinguish them, the former is usually called *ferrous* oxide, and the latter *ferric* oxide, which, combined with water, constitutes ordinary rust.

The black oxide usually contains one molecule of each oxide, so that it would be written $FeO.Fe_2O_3$, or Fe_3O_4. It is powerfully attracted by the magnet, and is often called magnetic oxide of iron. The abundant magnetic ore of iron, of which the *loadstone* is a variety, has a similar composition.

Iron in a very fine state of division takes fire spontaneously in air as certainly as phosphorus does. *Pyrophoric* iron can be obtained (by

a process to be described hereafter) as a black powder, which must be preserved in sealed tubes. When the tube is opened, and its contents thrown into the air, oxidation occurs, and is attended with a vivid glow. In this case the red oxide of iron is produced instead of the black oxide.

Both these oxides of iron are capable of neutralising, or partly neutralising, acids, and are therefore basic oxides or bases, like the oxides of zinc and sodium obtained in previous experiments. So general is the disposition of metals to form oxides of this class, that it may be regarded as one of the distinguishing features of a metal, for no non-metal ever forms a base with oxygen.

(DEFINITION.—A *metal* is an element capable of forming a base by combining with oxygen.)

Many metals are capable also of forming anhydrides with oxygen; thus, tin forms stannic anhydride (SnO_2), antimony forms antimonic anhydride (Sb_2O_5), and it is always found that a metallic anhydride contains a larger proportion of oxygen than any of the other oxides which the metal may happen to form.

27. There is a third class of oxides, termed the *indifferent oxides*, because they are neither anhydrides nor bases; such oxides may be formed either by non-metals or metals; thus water (H_2O), the oxide of hydrogen, is an indifferent oxide, and the black oxide of manganese (MnO_2) is an example of an indifferent metallic oxide.

As the most stable compound of oxygen with hydrogen, namely, water, has the formula OH_2, oxygen is the type of the divalent elements (p. 23).

28. *Preparation of oxygen.*—For almost all the useful arts in which uncombined oxygen is required, the diluted gas contained in atmospheric air is sufficient, since the nitrogen mixed with it does not interfere with its action.

From atmospheric air pure oxygen was first obtained by Lavoisier towards the end of the last century. His process is far too tedious to be employed as a general method of preparing oxygen, but it affords a very good example of the relation of heat to chemical action. Some mercury was poured into a glass flask with a long narrow neck, which was placed on a furnace, so that its temperature might be constantly maintained at about 349° C. (660° F.) for twelve days. The mercury boiled, and a portion of it was converted into vapour, which condensed in the neck of the flask and ran back again. Eventually part of the mercury was converted into a dark powder, which became red on cooling, having combined with the oxygen of the air (or undergone *oxidation*) to form the *red oxide of mercury.*

By heating this oxide of mercury to a temperature approaching a red heat (about 500° C. or 1000° F.) it is decomposed into mercury and oxygen gas ($HgO = Hg + O$).

It is very generally found, as in this instance, that heat of moderate intensity favours the operation of chemical attraction, whilst a more intense heat annuls it.

For the purpose of experimental demonstration, the decomposition of the oxide of mercury may be conveniently effected in the apparatus represented by Fig. 30, where the oxide is placed in the hard glass tube A, and heated by the gas-burner B, the metallic mercury being condensed in the bend C and the oxygen collected in the gas cylinder D, filled with water, and standing upon the bee-hive shelf of

the *pneumatic trough* E. It may be identified by its property of kindling into flame the spark left at the end of a wooden match. If the heat be continued for a sufficient length of time, the whole of the oxide of mercury will disappear, being resolved into its elements. In technical language, the mercury is said to be *reduced*. Upon the first application of heat the red oxide suffers a physical change, in consequence of which it becomes black ; but its red colour returns again if it be allowed to cool.

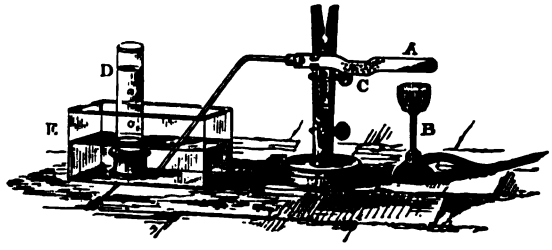


Fig. 30.—Preparation of oxygen from oxide of mercury.

This method of obtaining unmixed oxygen from the air is much too costly to be employed on a large scale.

Brin's process for preparing oxygen from the air depends upon the facts that when barium oxide (BaO) is heated in air it combines with oxygen, forming barium dioxide (BaO_2), and that when this latter is heated more strongly, or under diminished pressure, it gives up oxygen, again becoming BaO, thus :— (1) $BaO + O = BaO_2$; (2) $BaO_2 = BaO + O$. The original barium oxide is used again.

Air (purified from carbon dioxide) is pumped under pressure (10 lbs. per square inch) through retorts containing the barium oxide, heated at 700° C. ; when the issuing gas is no longer approximately pure nitrogen, the air current is stopped and the residual nitrogen in the retorts is pumped out until the pressure has fallen to about 2 lbs. per square inch. The barium dioxide then gives off much of its oxygen, which is collected in a gasholder. The cycle of operations is repeated.

Another process which has been used depends upon the principle that the oxides of manganese, when heated in contact with alkalies and air, are capable of absorbing the oxygen from the air, and of subsequently giving it up again if heated in a current of steam.

To illustrate this process, about four ounces of dry sodium manganate (which may be purchased cheaply in a crude state) are introduced into a porcelain tube * (*t*, Fig. 31) fixed in a furnace. One end of the tube is connected with a two-branched glass tube, so that either a current of air may be passed through it by the tube *a*, or a current of steam from the flask *w*. On heating the manganate in the tube to dull redness, and passing the steam over it, oxygen is evolved, and may be collected in the jar *o*.

$$\underset{\text{Sodium manganate.}}{2Na_2MnO_4} + \underset{}{2H_2O} = \underset{\text{Caustic soda.}}{4NaHO} + \underset{\text{Manganese sesquioxide.}}{Mn_2O_3} + O_3.$$

If the current of steam be discontinued and the air be slowly passed through the tube *a*, the oxygen of the air will be absorbed, and its nitrogen may be collected in the jar *n*.

$$4NaHO + Mn_2O_3 + 3\underset{\text{Air.}}{(O + N_4)} = 2Na_2MnO_4 + 2H_2O + N_{12}.$$

If the proper temperature be employed, the stream of gas issuing from the tube may be constantly kept up, and may be made to consist of oxygen or nitrogen accordingly as steam or air is passed through the tube. The current of air is regulated by the nipper-tap *c*.

The gas-furnace represented in Fig. 31 consists of a row of twelve Bunsen burners each having a stop-cock by which the flame is regulated. The horizontal pipe *b*,

* A copper tube with screw-caps, into which narrow brass or copper tubes are brazed may be advantageously substituted for the porcelain tube. The process is much facilitated by mixing the manganate of soda with an equal weight of oxide of copper.

from which they spring, is capable of being raised or lowered at pleasure. The porcelain tube *t* is laid in a semi-cylindrical trough made of stout iron rods, and filled with pieces of pumice-stone or fire-brick. Above this is placed a corresponding trough, so that the tube is entirely surrounded by glowing material. The heat must be applied gradually to avoid splitting the tube.

Fig. 31.—Extraction of oxygen from air.

Oxygen is now obtained approximately free from nitrogen by a physical method which takes advantage of the fact that nitrogen has a lower boiling-point than oxygen, so that when the temperature of liquid air (p. 74) is slowly raised the nitrogen boils away before the oxygen.

29. The only other natural source from which it has been found convenient to prepare pure oxygen, is a black mineral composed of manganese and oxygen. It is found in some parts of England, but much more abundantly in Germany and Spain, whence it is imported for the use of the bleacher and glassmaker. Its commercial name is *manganese*, but it is known to chemists as *binoxide of manganese* or *manganese dioxide* (MnO_2), and to mineralogists by several names designating different varieties. The most significant of these names is *pyrolusite*, referring to the facility with which it may be decomposed by heat ($\pi\hat{\upsilon}\rho$, fire, and $\lambda\acute{\upsilon}\omega$, to loosen).

One of the cheapest methods of preparing oxygen consists in heating small fragments of this black oxide of manganese in an iron retort, placed in a good fire, the gas being collected in jars filled with water, and standing upon the shelf of the pneumatic trough, or in a gas-holder or gas-bag, if large quantities are required.

The attraction existing between manganese and oxygen is too powerful to allow the metal to part with the whole of its oxygen when heated, so that only one-third of the oxygen is given off in the form of gas, a brown oxide of manganese being left in the retort: $3MnO_2 = Mn_3O_4 + O_2$.

30. By far the most convenient source of oxygen, for general use in the laboratory, is the artificial salt called *chlorate of potash*, or *potassium chlorate*, which is largely manufactured for fireworks, percussion-cap composition, &c. If a few crystals of this salt be heated in a test-tube over a spirit lamp (Fig. 32) they soon melt (360° C.) to a clear liquid,

which presently begins (400° C.) to boil from the disengagement of bubbles of oxygen, easily recognised by introducing a match with a spark at the end into the upper part of the tube. If the action of heat is continued until no more oxygen is given off, the residue in the tube is the salt termed potassium chloride;

Fig. 32.

$$KClO_3 = KCl + O_3.$$

Potassium chlorate. Potassium chloride.

To ascertain what quantity of oxygen would be furnished by a given weight of the chlorate, the atomic weights must be brought into use. Referring to the table of atomic weights, it is found that K = 39, O = 16 and Cl = 35.5; hence the molecular weight of potassium chlorate is easily calculated.

One atomic weight of potassium	39
" " chlorine	35.5
Three atomic weights of oxygen	48
$KClO_3$ =	122.5

So that 122.5 grams of chlorate would yield 48 grams of oxygen.

Since 16 grams of oxygen (more accurately 15.88) measure 11.11 litres (p. 32), the 48 grams will measure 33.33 litres.

Hence it is found that 122.5 grams of potassium chlorate would give 33.33 litres of oxygen measured at 0° C. and 760 mm. Bar.

Since the complete decomposition of the potassium chlorate requires a more intense heat than a glass vessel will usually endure, it is customary to mix the chlorate with about one-fifth of its weight of powdered black oxide of manganese, when the whole of the oxygen is given off at a comparatively low temperature (about 360° C.), though the oxide of manganese itself suffers no change, and its action has not yet received any explanation which is quite satisfactory.

Fig. 33 shows a very convenient arrangement for preparing and collecting oxygen for the purpose of demonstrating its relations to combustion. A is a

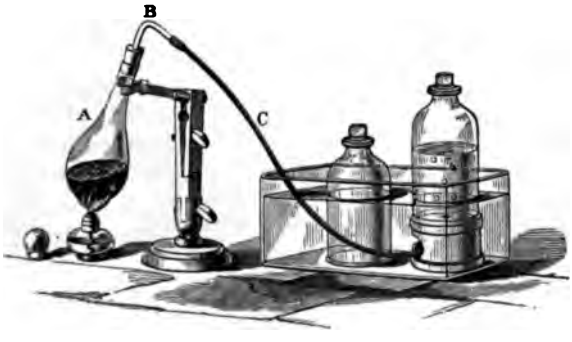


Fig. 33.—Preparation of oxygen.

Florence flask in which the glass tube B is fixed by a perforated cork. C is a tube of vulcanised india-rubber. The gas-jar is filled with water, and supported upon a bee-hive shelf. If pint gas-jars be employed, 20 grams of potassium

chlorate, mixed with 4 grams of binoxide of manganese, will furnish a sufficient supply of gas for the ordinary experiments. The binoxide of manganese should be thoroughly dried by moderately heating it in a crucible before being mixed with the chlorate. It is also advisable to test it by heating a little of it with the chlorate, since charcoal and sulphuret of antimony, which form very explosive mixtures with chlorate of potash, have sometimes been sold by mistake for binoxide of manganese. The heat must be moderated according to the rate at which the gas is evolved, and the tube C must be taken out of the water before the lamp is removed, or the contraction of the gas in cooling will suck the water back into the flask. The first jar of gas will contain the air with which the flask was filled at the commencement of the experiment. The oxygen obtained will have a slight smell of chlorine.

WATER.

$H_2O = 18$ grams = 2 volumes (vapour).

31. *Synthesis of water from its elements.*—It has been seen already (p. 30) that the combination of hydrogen with oxygen to form water is attended with great evolution of heat and consequent expansion, and hence the mixture of these gases is found to explode violently on contact with flame.

The experiment may be made safely in a soda-water bottle (old form). The bottle is filled with water, and inverted with its mouth beneath the surface of the water; enough oxygen is then passed up into it to one-third of its volume; if the remainder of the water is then displaced by hydrogen, and the mouth of the bottle presented to the flame of a spirit-lamp, a very violent explosion occurs, attended with a vivid blue flash in the bottle. If the mouth of the bottle be presented towards a screen of paper, at a distance of 20 or 30 inches, the paper will be violently torn to pieces, bearing witness to the concussion between the expanded steam issuing from the bottle and the external air.

If some of the mixture of oxygen with twice its volume of hydrogen be introduced into a jar provided with a stop-cock to which is attached a piece of caoutchouc tubing and a small glass tube, and if the jar be pressed down in a

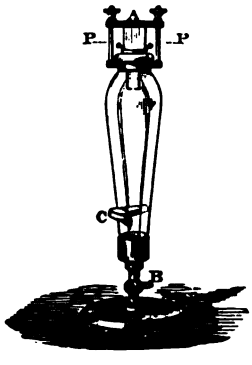


Fig. 34.

Fig. 35.

trough of water, soap-bubbles may be inflated with the gas, and these will ascend rapidly in the air, and explode violently when touched with a flame, which must not, of course, be applied to the bubble until it is at some distance away, from the tube, for fear of exploding the mixture in the jar.

The mixture of 2 volumes H and 1 volume O explodes when heated to 600° C, but it may be exposed to a temperature of over 1000° C. without the occurrence of

any combination if it be carefully dried, by freshly distilled phosphoric anhydride, in the dark. The precaution to exclude light is essential because the moist gases combine even at the ordinary temperature when exposed to light, and although the combination is extremely slow, the amount of water produced thereby is sufficient to ensure explosion at 600° C.*

Contact with finely divided platinum starts the combination of H and O at the ordinary temperature, and a red hot platinum wire causes even the dried gases to explode. Electric sparks also explode the dried gases.

32. In order to demonstrate the production of water in the explosion, the *Cavendish eudiometer*† (Fig. 34) is employed. This is a strong glass vessel, with a stopper firmly secured by a clamp (A), and provided with two platinum wires (P), which pass through the stopper, and approach very near to each other within the eudiometer, so that the electric spark may easily be passed between them. By screwing the stop-cock B into the plate of an air-pump, the eudiometer may be exhausted. It is then screwed on to the jar represented in Fig. 35, which contains a mixture of two measures of hydrogen with one measure of oxygen, standing over water. On opening the stop-cocks between the two vessels, the eudiometer becomes filled with the mixture, and the quantity which has entered is indicated by the rise of water in the jar. The glass stop-cock C having been closed to prevent the brass cap from being forced off by the explosion, the eudiometer is again screwed on to its foot, and an electric spark passed between the platinum wires, either from a Leyden jar or an induction coil, when the two gases will combine with a vivid flash of light,‡ attended with a very slight concussion, but no noise, since there is no collision with the external air. For an instant a mist is perceived within the eudiometer, which condenses into fine drops of dew, consisting of the water formed by the combination of the gases, which was here induced by the high temperature of the electric spark, as it was in the former experiment by the high temperature of the flame. If the gases have been mixed in the exact proportion of two measures of hydrogen to one measure of oxygen, the eudiometer will now be again vacuous, and if it be screwed on to the capped jar, may be filled a second time with the mixture, which may be exploded in the same manner.

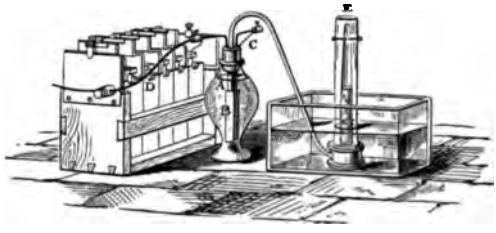


Fig. 36.—Detonating gas collected from voltameter.

The entire disappearance of the gases may be rendered obvious to the eye by exploding the mixture over mercury. For this purpose the mixed gases should be collected from water itself, which is strongly acidified with sulphuric acid, and decomposed in the *voltameter* (A, Fig. 36) by the aid of five or six cells of Grove's battery. The voltameter contains two platinum plates (B), attached to the platinum wires C and D, which are connected with the opposite poles of the battery. The first few bubbles of the mixture of hydrogen and oxygen evolved having been allowed to escape, in order to displace the air, the gas may be collected in the small eudiometer (E), which has been previously filled with water. This eudiometer is a cylinder of very thick glass,§ closed at one end, and having two stout platinum wires cemented into holes drilled near the closed end, the wires approaching sufficiently near to each other to allow the passage of the electric spark. Having been filled with the mixture of hydrogen and oxygen from the

* In these experiments very pure electrolytic gas made by electrolysing a solution of purified barium hydroxide was used.

† So named from εὖδιος, fine or clear, and μέτρον, a measure, because an instrument upon the same principle has been used to determine the degree of purity of the atmosphere. The eudiometer was employed by Cavendish about the year 1770, for the synthesis of water.

‡ Since the steam produced at the moment of combination is here prevented from expanding, the heat which would have expanded it is saved, so that the *temperature* is higher and the flash of light brighter than when the combination is effected in an open vessel.

§ The bore of the eudiometer should be about half an inch in diameter, and the thickness of its sides about $\frac{1}{8}$ths of an inch; its length is 7 inches.

voltameter, the eudiometer is closed with the finger, and transferred to a basin containing mercury, where it is pressed firmly down upon a stout cushion of india-rubber, and the spark passed through the mixed gases, either from the coil or the Leyden jar. The combustion occurs with violent concussion, but without noise; and since the eudiometer is vacuous after the gases have combined, the cushion will be found to be very firmly pressed against its open end. On loosening the cushion, the mercury will be violently forced up into the eudiometer, which will be completely filled with it, proving that when an electric spark is passed through the mixture of 2 volumes of hydrogen and 1 volume of oxygen, no residue of gas remains.

This may also be demonstrated with the siphon eudiometer, shown in Fig. 37, by confining about a cubic inch of the explosive mixture in the closed limb, over water, and stopping the open limb securely with a cork, so as to leave a space filled with air between the cork and the water. The eudiometer must be very firmly fixed on a stand, or it will be broken by the concussion. After it has been proved, it may be held in the hand, as in the figure. By firing mixtures of hydrogen and oxygen, in different proportions, in the same manner, it may be shown that any excess of either gas above the ratio of 2H : O will remain uncombined after the explosion. Care is required in these experiments, since eudiometers are often burst by the explosion of the mixture of 2 volumes of hydrogen with 1 volume of oxygen.

The explosion and the flash of light in the foregoing experiments are both the results of the heat generated in the act of combination; so that the water produced represents so much less *energy* as corresponds with the heat given off in the combination. This heat has been measured by means of a *calorimeter*, and it has been found that 2 grams of H and 16 grams of O, in combining to form liquid water, generate enough heat to raise 68,924 grams of water from 0° C. to 1° C. Of this quantity, 9666 represent the heat generated by the change of state from the gas to the liquid, so that the difference, 59,258, represents the heat generated by the chemical action occurring between 2 grams of hydrogen and 16 grams of oxygen in forming 18 grams of water in the state of gas. This may be expressed by $H_2 + O = H_2O + 59{,}258$ *heat-units*, the heat-unit being the quantity of heat required to raise the temperature of 1 gram. of water from 0° C. to 1° C.

The quantity of heat produced in any chemical action is a measure of the amount of chemical energy which is exerted. To decompose 18 grams of steam we must employ an amount of energy, in the form, for example, of electricity, corresponding with 59,258 heat-units. (See chapter on General Principles.)

33. The knowledge of the volumes in which hydrogen and oxygen combine, is turned to account in the analysis of gases, to ascertain the proportion of hydrogen or oxygen contained in them. Suppose, for example, it be required to determine the amount of oxygen in a sample of atmospheric air; the latter is mixed with hydrogen, in more than sufficient quantity to combine with the largest proportion of oxygen which could be present, and when the combination has been induced by the electric spark, the volume of gas which has disappeared (2 volumes H + 1 volume O) has only to be divided by three to give the volume of the oxygen.

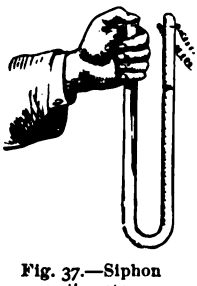


Fig. 37.—Siphon eudiometer.

A bent eudiometer (Fig. 37) may be used. Having been completely filled with water (previously boiled to expel dissolved air), it is inverted in the trough, and the specimen of air is introduced (say 10 c.c.). The open limb is then closed by the thumb, and the eudiometer turned so as to transfer the air to the closed limb. A stout glass rod is thrust down the open limb, so as to displace enough water to equalise the level in both limbs, in order that the volume of the air may not be diminished by the pressure of a higher column of water in the open limb. The volume of the included air having been accurately noted, the open limb of the tube is again filled up with water, inverted in the trough, and a quantity of hydrogen introduced, equal to about half the volume of the air. This having been trans-

ferred, as before, to the closed limb, the columns of water are again equalised, and the volume of the mixture of air and hydrogen ascertained. The open limb is now firmly closed with the thumb, and the electric spark passed through the mixture, either from the Leyden jar or the induction-coil. On removing the thumb, after the explosion, the volume of gas in the closed limb will be found to have diminished very considerably. Enough water is poured into the open limb to equalise the level, and the volume of gas is observed. If this volume be subtracted from the volume before explosion, the volume of gas which has disappeared will be ascertained. and one-third of this will represent the oxygen, which has condensed with twice its volume of hydrogen into the form of water. Thus the numbers recorded will be—

Volume of air analysed	10 c.c.
Volume of air mixed with hydrogen	15 „
After explosion	9 „
Difference ($\frac{2}{3}$H and $\frac{1}{3}$O)	6.0 „

6 divided by 3 = 2 c.c. of oxygen.

In exact experiments, a correction would be required for any variation of the temperature or barometric pressure during the progress of the analysis.

34. It will have been observed, in the experiment upon the synthesis of water in the Cavendish eudiometer, that the volume of water obtained is very small in comparison with that of the gases before combination, about 1870 volumes of the mixed gases being required to form one volume of liquid water, because after the *chemical* attraction has caused the molecules of H and O to form steam, the *cohesive* attraction has caused the molecules of steam to unite and form liquid water. In order to watch the effect of the chemical attraction only, we must prevent the steam from changing its state after it is produced.

If the mixture of hydrogen and oxygen be measured and exploded at or above the boiling-point of water, it is found that the steam produced occupies two-thirds of the volume of the mixed gases, measured at the same temperature and atmospheric pressure. Hence, *two volumes of hydrogen combine with one volume of oxygen to form two volumes of aqueous vapour, at the same temperature and pressure.**

Fig. 38.—Synthesis of water at 100° C.

The combination of hydrogen and oxygen in a vessel heated to the boiling-point of water is effected in the apparatus shown in Fig. 38, where the closed limb of the eudiometer is surrounded by a tube into which steam is passed from a flask connected with the wide tube by a cork and a short wide piece of bent glass tubing, jacketed with caoutchouc to prevent loss of heat. The steam escapes through the tube (*t*) which enters the cork at the bottom. The closed limb of the eudiometer having been filled with mercury, a small quantity of the mixture of hydrogen and oxygen obtained from the voltameter (Fig. 36) is introduced into it through a tube passed down the open limb, the displaced mercury being run out through the tube *c*, which is closed by a nipper-tap. The closed limb is then heated by the steam, and the mercury in the two limbs levelled from time to time by running a little out through *c*, until the gas in the closed limb no longer expands. Its volume is then

* The latest researches show that the exact volume ratio is 2.0024 H : 1 O.

observed, an inch more mercury poured into the open limb, which is then tightly closed by a cork, and the spark from the induction-coil (Fig. 8) is passed by the wires – and +. After the explosion, the cork is removed, and the mercury levelled in the two limbs, when the volume of the steam will be found to be just two-thirds of the volume of the gas before the explosion. On cooling down, the steam condenses, and the mercury entirely fills the closed limb of the eudiometer.

That 2 volumes of steam should contain 2 volumes of hydrogen and 1 volume of oxygen would appear, on physical grounds, impossible, since two bodies cannot occupy the same space at the same time; but it must be remembered that the two bodies in question have lost their individuality in consequence of their chemical combination by which they have become one body—water.

35. The synthesis of water by weight is difficultly effected with accuracy by weighing the gases themselves, on account of their large volume. It is therefore accomplished by passing an indefinite quantity of hydrogen over a known weight of pure hot oxide of copper, when the hydrogen combines with the oxygen of the oxide to form water. The loss of weight suffered by the oxide of copper gives the amount of oxygen; and if this be deducted from the weight of the water, that of the hydrogen will be ascertained. In this way it is shown that water contains 8 parts of oxygen to every 1 part of hydrogen.*

The apparatus employed for this purpose is represented in Fig. 39. *h* is the bottle in which hydrogen is generated from diluted sulphuric acid and zinc; the gas passes, in *p*, through solution of potash, which absorbs any sulphuretted hydrogen; then through *s*, containing pumice-stone (used on account of its porous character), saturated with a strong solution of silver nitrate, which removes

Fig. 39.—Synthesis of water by weight.

arsenic and antimony from the hydrogen; the gas then passes through *vv*, containing pumice saturated with oil of vitriol to absorb moisture. The bulb *c*, with the oxide of copper, is weighed before and after the experiment, as are the globe *g*, for condensing the water, and the tube *t*, containing pumice and oil of vitriol, to absorb the aqueous vapour. Of course the bulb *c* must not be heated until the hydrogen has displaced all the air from the apparatus.

As an example, 10 grams of CuO were employed, and 7.98 grams Cu were left, 2.2725 grams water being collected. $10-7.98=2.02$ grams O; $2.2725-2.02=0.2525$ grams H; 2.2725 : 2.02 : : 100 : 88.88; 2.2725 : 0.2525 : : 100 : 11.11. 100 parts by weight of water, therefore, contain 88.88 O and 11.11 H. This is the usual method of stating the composition of a substance. To deduce the chemical formula, we must divide each constituent by its atomic weight; $88.88\div 16=5.5$ atomic weights of O; $11.11\div 1=11.11$ atomic weights of H. Then 5.55 : 11.11 : : 1 atom O : 2 atoms H.

The above experiment would also serve for fixing the atomic weight of copper, for it shows that 100 parts by weight of cupric oxide contains 79.8 parts of copper and 20.2 parts of oxygen. Then 20.2 : 79.8 : : 16 : 63.2; so that if cupric oxide

* The latest value for this ratio is 7.94 O : 1 H.

contains one atom of copper to one atom of oxygen, the atomic weight of copper would be 63.2.

35*a*. A volume of steam is found to weigh 9 times as much as an equal volume of hydrogen weighs at the same temperature and pressure. Now, evidence (the value of which will be better appreciated after more experimental facts have been described) has been gathered, from both the chemical and physical study of gases, that *equal volumes of gases measured at the same temperature and pressure contain the same number of molecules* (Avogadro's Law). It follows that the number of times that a volume of one gas, A, is heavier than a volume of another gas, B, is also the number of times that each molecule in A is heavier than each molecule in B.* Consequently the molecule of steam weighs 9 times as much as the molecule of hydrogen; but the molecule of hydrogen contains 2 atoms, and therefore weighs two units, so the molecule of steam must weigh 18 units. It is by similar reasoning that that the molecular weights of all gases are decided. (*See* Introduction.)

It will now be understood that the formula for a compound is determined both by a *quantitative analysis* or quantitative *synthesis* of the compound, and by ascertaining its specific gravity when H = 1 (its *vapour density*).

A quantitative synthesis of water shows that it contains H and O in the proportion of 1 : 8; a determination of its vapour density shows that its molecular weight is 18: hence its formula must be H_2O, which is in agreement with the proportion 1 : 8 (2 : 16), and with the molecular weight 18 (2 + 16).

It has been seen (p. 24) that one gram of hydrogen occupies (at standard temperature and pressure) 11.11 litres, so that 2 grams occupy 22.22 litres. As the molecular weight of a gas is the number of times that it is heavier than 2 unit weights of hydrogen, it follows that *the molecular weight of any gas expressed in grams occupies 22.22 litres at standard temperature and pressure.*

36. It is evident that, although hydrogen is generally designated the combustible gas, and oxygen the supporter of combustion, the application of these terms depends entirely upon circumstances, since the phenomenon of combustion is a reciprocal operation in which both elements have an equal share.

This may be illustrated by a simple experiment. The hydrogen and oxygen reservoirs, **H** and **O**, Fig. 40, are connected with two bent glass tubes passing through a cork into an ordinary lamp glass *c*, upon the upper opening of which a plate of talc is laid. In order to prevent the ends of the glass tubes from being fused by the burning gases, little platinum tubes, made by rolling up pieces of platinum foil, are placed in the orifices, and the glass is melted round them by the blowpipe flame. The hydrogen being lighted, and the oxygen turned on to about the same extent, the lamp-glass is placed over the cork, when the hydrogen burns steadily. If the oxygen be slowly turned off, the flame will gradually leave the hydrogen tube and come over to the oxygen, which will continue burning in the atmosphere of hydrogen. By again turning on the oxygen, the flame may be sent over to the hydrogen tube. With a little care the flame may be made to occupy an intermediate position between the two burners, and to leap from one to the other at pleasure. The experiment may also be performed with coal gas and oxygen.

* This is, of course, only true if all the molecules in a gas have each the same weight. There is no reason to suppose that the molecules of any one gas differ appreciably from each other in weight, but even if they did the argument would be true of the *mean* weight of each molecule, *i.e.*, the weight of the gas divided by the number of molecules in it.

37. **The great energy with which hydrogen combines with oxygen is turned to account for the purpose of producing very high temperatures (about 2500° C.)**

The *oxyhydrogen* blowpipe (Fig. 41) is an apparatus for burning a jet of hydrogen mixed with half its volume of oxygen. The gases are supplied from separate gas-holders (or bags with pressure-boards and weights) through the tubes H and O, which conduct them into the brass sphere B. Each of these tubes is provided with a valve of oiled silk opening outwards, so as to prevent the passage of either gas into the receptacle containing the other. The tube A is stuffed with thin copper wires, which would rapidly conduct away the heat and extinguish the

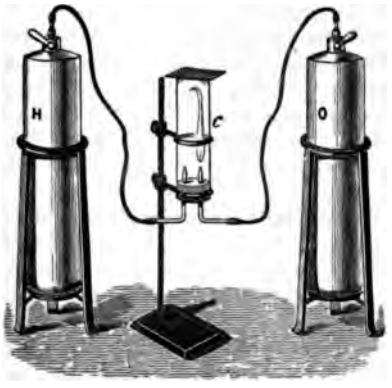


Fig. 40.—Reciprocal combustion.

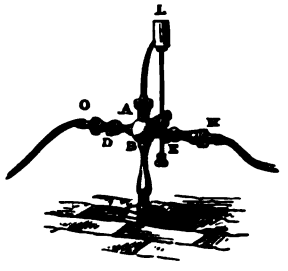


Fig. 41.—Oxyhydrogen blowpipe.

Fig. 42.

flame of the mixed gases burning at the jet, should it tend to pass back and ignite the mixture in B. The stop-cocks D and E allow the flow of the gases to be regulated so that they may mix in the right proportions. If the hydrogen be kindled first, it will be found that, as soon as the oxygen is turned on, the flame is reduced to a very much smaller volume, because the undiluted oxygen required to maintain it occupies only one-fifth of the volume of the atmospheric air, from which the hydrogen was at first supplied with oxygen. The heat developed by the combustion being therefore distributed over a much smaller area, the temperature at any given point of the flame must be much higher, and very few substances are capable of enduring it without fusion.* Lime is one of these ; and if a cylinder of lime be supported, as at L (Fig. 41), in the focus of the flame, its particles become heated to incandescence, and a light is obtained which is visible at night from very great distances, so as to be well adapted for signalling and lighthouses. For such purposes coal-gas is often used instead of hydrogen (*oxycalcium* or *Drummond* light).

If a shallow cavity be scooped in a lump of quicklime, a few scraps of platinum placed in it, and exposed to the oxyhydrogen flame (Fig. 42), a fused globule of platinum of very considerable size may be obtained in a few seconds. By employing a furnace made of lime, platinum is fused in quantities sufficient to cast large ingots, a result unattainable by any other furnace heated by combustion. Pipeclay, which resists the action of all ordinary furnace-heats, may be fused into a glass in this flame, whilst gold and silver are instantaneously melted, and vaporised into a dense smoke.

* The temperature of the hydrogen flame in air is about 2000° C., while in oxygen it is over 2500°. The last temperature could not be surpassed, because it is that at which steam is *dissociated* or resolved into its elements, which re-combine as soon as the temperature falls below that point.

38. In its chemical relations to other elements, hydrogen is diametrically opposed to oxygen. Whereas the latter combines directly with the greater number of the elements, hydrogen will enter into direct combination with very few; all the metals form compounds with oxygen, but very few combinations of metals with hydrogen have been obtained. Indeed, in its relations to other elements, hydrogen closely resembles the metals, though it does not fall within the definition of a metal given above, since it does not form a base with oxygen, and its combinations with the salt radicles (chlorine, &c.) are acids, and not salts, as is the case with metals.

Hydrogen is absorbed, or *occluded*, by many metals to a greater extent than are most other gases, and by palladium more than by any other metal. This phenomenon of *occlusion*, which may be compared with that of solution, generally occurs more readily when the metal is heated, and allowed to cool, in the gas; when treated in this way hammered palladium absorbs some 600 times its volume of hydrogen, though fused palladium does not absorb so much. When a metal containing occluded gas is strongly heated (particularly in a vacuum or in an atmosphere of another gas), the occluded gas is given off, just as a gas dissolved in water is expelled when the solution is heated. Palladium absorbs most hydrogen when it is used as the cathode in an electrolytic cell containing dilute acid (p. 14). In this case the metal may take up about 900 times its volume, and in doing so it increases about 1.5 per cent. in length. This expansion forms the basis of experimental methods for demonstrating the occlusion. A palladium wire (24 inches) is passed through the bottom cork of a vertical glass tube, containing dilute sulphuric acid, and is there made fast; the other end of the wire is attached to a long rod, pivoted horizontally to serve as an index. The wire is attached to the zinc of a Grove's battery, the platinum of the battery being attached to a platinum wire which also passes through the glass tube. During the electrolysis of the dilute sulphuric acid, the index descends, showing that the wire is increasing in length; the non-recovery of the index when the electrolysis is stopped shows that the expansion was not a mere thermal effect.

It has been supposed that the palladium saturated with hydrogen is a compound of the formula Pd_2H_2.* The hydrogenised palladium is a far more active reducing agent than is free hydrogen, for it reduces chlorates to chlorides and nitrates to nitrites. If the whole of the hydrogen be regarded as being occluded, its specific gravity in this condition would be 0.62, and its atomic heat 5.88. The absorption of 1 gram of hydrogen by palladium black evolves 4370 gram units of heat. At atmospheric pressure no absorption of hydrogen by palladium occurs above 145° C., but at higher pressures the absorption occurs at much higher temperatures.

39. *Chemical relations of water to other substances.*—In its chemical relations water presents this very remarkable feature, that, although it is an *indifferent oxide*, its combining tendencies extend over a wider range than those of any other compound. Its combinations with other substances are generally called *hydrates*. Water combines with two of the elementary substances, viz., chlorine and bromine, but no other element is even dissolved by water in any considerable quantity. Oxygen, hydrogen, and nitrogen are dissolved by water, in very small quantity, but become only mechanically diffused through it, and do not enter into chemical combination.

When water attacks a compound body, it may do so in one of two ways: (1) A *simple solution* may be effected. In this case any chemical combination which may occur between the compound and the water is of so loose a nature that it is possible to recover the compound unchanged by merely evaporating the water. (2) The water may combine

* The term *hydrogenium*, applied by Graham to the hydrogen occluded by palladium, on the supposition that it existed merely in a state of condensation in the metal, must be abandoned if the existence of this compound be admitted.

with the compound to produce a new compound of such stability that the original substance cannot be recovered by mere evaporation. The new compound may then pass into simple solution.

It might at first be thought that simple solution was only a physical phenomenon, since there is no permanent alteration in the properties of the dissolved substance. This view would be supported by the observation that when a solid is dissolved, there is a reduction of temperature, such as is always noticed in the merely physical change from the solid to the liquid form; and that when a gas is dissolved there is a rise of temperature such as is noticed when a gas passes to the liquid form. When careful measurements are made, however, it is found that the thermal change involved in the dissolution cannot be entirely accounted for by the physical change of state. Consequently it must be allowed that chemical combination is concerned in the process of dissolution although the most obvious relations produced are of a physical nature. At this juncture attention will be called to the principal facts concerning solution, a discussion of the deductions to be drawn from them being for the present postponed.

When common saltpetre (nitre or nitrate of potash) is shaken with water, it is rapidly dissolved, the water becoming sensibly colder. If fresh portions of saltpetre are added till the water is unable to dissolve any more, it is found that 100 grams of water (at 60° F.) have dissolved about 30 grams of saltpetre. Such a solution is a *cold saturated solution* of saltpetre. If the solution be set aside in an open vessel, the water will slowly pass off in vapour, and the saltpetre will be gradually deposited, its particles arranging themselves in the regular geometrical shape of the six-sided prism, which is its common *crystalline form*. The crystals of saltpetre do not contain any water; they are *anhydrous*.

If saltpetre is added to boiling water, and stirred (with a glass rod) until the water refuses to dissolve any more, 100 grams of water is found to have dissolved about 200 grams; this is a *hot saturated solution*.

As a general rule, solids are dissolved more quickly and in larger quantity by hot water than cold.

One of the commonest methods of *crystallising* a solid substance consists in dissolving it in hot water and allowing the solution to cool slowly. The more slowly it cools, the larger and more symmetrical are the crystals.

A hot saturated solution is not generally the best for crystallising, because it deposits the dissolved body too rapidly. Thus the hot solution of saltpetre prepared as above would solidify to a mass of minute crystals on cooling; but if 100 grams of saltpetre be dissolved in 120 c.c. of boiling water, it will form crystals of 2 or 3 inches long when slowly cooled (in a covered vessel). If the solution be stirred while cooling, the crystals will be very minute, having the appearance of a white powder.

Some solids, however, refuse to crystallise, even from a hot saturated solution, if it be kept absolutely undisturbed.

Sodium sulphate affords a good example of this. If the crystallised sulphate be added to boiling water in a flask, as long as it is dissolved, the water will take into solution more than twice its weight of the salt, yielding a solution which boils at 220° F. (104.5° C.). If this solution be allowed to cool in the open flask, an abundant crystallisation will occur, for cold water dissolves only about one-third of its weight of crystallised sulphate. But if the flask (which should be globular) be tightly

corked whilst the solution is boiling, it may be kept for several days without crystallising, although moved about from one place to another. In this condition the solution is said to be *super-saturated*. On withdrawing the cork, the air entering the partly vacuous space above the liquid will be seen to disturb the surface slightly, and from that point beautiful prismatic crystals will shoot through the liquid until the whole has become a nearly solid mass. A considerable elevation of temperature is observed, consequent upon the passage from the liquid to the solid form. If the solution of sodium sulphate be somewhat weaker, containing exactly two-thirds of its weight of the crystals, it may be cooled without crystallising, even in vessels covered with glass plates, but a touch with a glass rod will start the crystallisation immediately.

The crystallisation of a supersaturated solution is provoked by contact with a crystal of the salt itself. Minute crystals of sodium sulphate are present in the floating dust of the air, and cause the crystallisation when they fall into the supersaturated solution. A perfectly clean glass rod may be dipped into the liquid without causing crystallisation, but a rod which has been exposed to air will have some particles of sodium sulphate on it, and will start crystallisation; if the rod be heated so as to render the sodium sulphate from the dust anhydrous, it will no longer cause crystallisation unless it be drawn through the hand. Air filtered through cotton-wool does not cause supersaturated solutions to crystallise. If the solution of sodium sulphate containing two-thirds of its weight of the crystals be allowed to cool in a flask closed by a cork furnished with two tubes plugged with cotton-wool, it will be found that, on withdrawing the plugs and blowing through one of the tubes dipping into the solution, no crystallisation occurs; but if air be blown by a pair of bellows into the same solution, it will crystallise at once.

Sodium hyposulphite (thiosulphate) and sodium acetate yield supersaturated solutions which are less likely to be crystallised by dust than the sodium sulphate. If a warm supersaturated solution of sodium acetate be very carefully poured upon a cold supersaturated solution of sodium hyposulphite, in a narrow cylinder, which is then covered and allowed to cool, a crystal of the hyposulphite may be dropped in without causing crystallisation till it reaches the lower layer of hyposulphite solution: a crystal of sodium acetate may then be dropped in to start the crystallisation of the upper layer.

Supersaturated solution of sodium acetate is used in railway foot-warmers, where the heat evolved in the crystallisation renders it four times as efficacious as the same volume of hot water.

A most beautiful illustration of the power of unfiltered air to start crystallisation is afforded by a solution of alum which has been dissolved in half its weight of water at 194° F. (90° C.) and allowed to cool in a flask, the mouth of which is closed by a plug of cotton-wool. In this state it may be kept for weeks without crystallising, but, on withdrawing the plug, crystallisation will be seen to start at a few points on the surface immediately under the opening of the neck, and will spread slowly from these, octahedral crystals of alum of half an inch or more in diameter being built up in a few seconds, the temperature, at the same time, rising very considerably.

In the laboratory, stirring is always resorted to in order to induce crystallisation, if it does not occur spontaneously. Thus it is usual to test for potassium in a solution by adding tartaric acid, which should cause the formation of minute crystals of *hydro-potassium tartrate* (*cream of tartar*), but the test seldom succeeds unless the solutions are briskly stirred together with a glass rod. An amusing illustration of this is afforded by pouring a solution of tartaric acid into a solution of saltpetre, and allowing the clear mixture to run over a large plate of glass. Letters traced on the glass with the finger will now be rendered visible by the deposition of the crystals of the tartrate upon the glass.

39A. Every crystal may be referred to one of comparatively few types, although the identification of the parent form of a crystal is not always easy, and is an art in itself, known as crystallography.

The classification of crystals is based on the symmetry of their faces around a plane or an axis drawn through the crystal. A plane of symmetry in a geometrical form is a plane dividing the form in such a manner that the two parts have the relationship of object and image to each other. When a crystal is turned round on a certain axis, it must be rotated through a certain angle before it appears again of the same form to the observer; accordingly as the rotation is through $\frac{1}{2}$, $\frac{1}{3}$, $\frac{1}{4}$ or $\frac{1}{6}$ of 360°, the crystal is said to have a 2-, 3-, 4-, or 6-fold axis of symmetry.

The following are the principal fundamental forms, and their parent geometrical figures are indicated in Fig. 43 by corresponding numbers :—(1) *Triclinic*, derived from an acute-angled parallelopipedon and devoid of symmetry. (2) *Monoclinic*, having one plane of symmetry and derived from a parallelopipedon with four rectangular and two acute-angled faces. (3) *Rhombic*, derived from a rectangular parallelopipedon, and having two planes of symmetry at right angles to each other. (4) *Quadratic*, having a four-fold axis of symmetry, and derived from a rectangular parallelopipedon with a square base. (5) *Trigonal*, having a three-fold axis of symmetry, and derived from a right triangular prism. (6) *Hexagonal*, having a six-fold axis of symmetry, and derived from a right hexagonal prism. (7) *Regular*, derived from the cube, and having three two-fold axes of symmetry at right angles to each other.

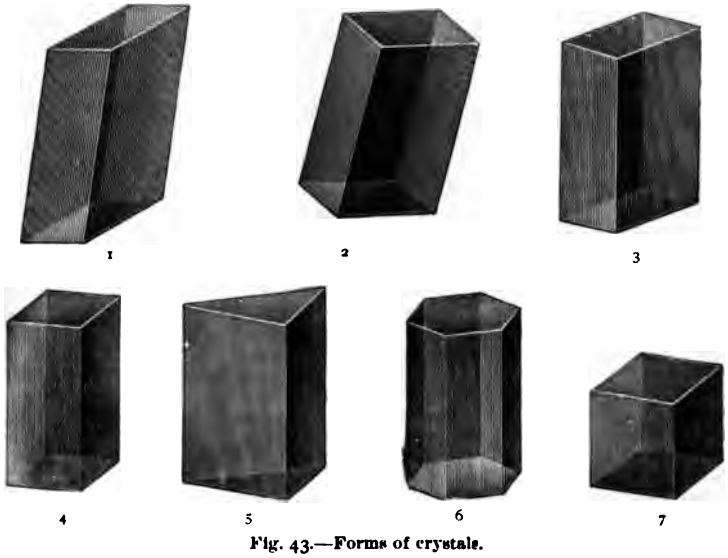


Fig. 43.—Forms of crystals.

40. Crystals of sodium sulphate contain, in a state of combination with the salt, more than half their weight of water. Their composition is—

Anhydrous sodium sulphate (Na_2SO_4) 142 parts, or one molecule ;
Water . . . . . 180 „ or ten molecules,

as expressed by the formula $Na_2SO_4.10H_2O$. If the crystals are left exposed to the air, they gradually *effloresce*, or become covered with a white opaque powder. This powder is the anhydrous sodium sulphate into which the entire crystals would ultimately become converted by exposure to air. Since most crystals containing water have their crystalline form destroyed or modified by the loss of the water, it is commonly spoken of as *water of crystallisation*.

Coloured salts, containing water of crystallisation, generally change colour when the water is removed. The *sulphate of copper* (*blue stone*) affords an excellent example of this. The beautiful blue prismatic crystals of this salt contain—

Anhydrous sulphate of copper ($CuSO_4$) 159.5 parts, or one molecule :
Water . . . . . 90 „ or five molecules,

as expressed by the formula $CuSO_4.5H_2O$.

When these are exposed to the air at the ordinary temperature they remain unchanged; but if heated to the boiling-point of water they become opaque, and may be easily crumbled down to a nearly white powder. This powder contains—

Anhydrous sulphate of copper ($CuSO_4$) 159.5 parts, or one molecule;
Water . . . . . 18 „ or one molecule,

and would therefore be represented by $CuSO_4.H_2O$. The four molecules of water, which have been expelled, constituted the water of crystallisation, upon which the form and colour of the sulphate of copper depend. When the white powder is moistened with water, combination occurs with great evolution of heat, and the blue colour is reproduced. The one molecule of water which still remains is not expelled until the salt is heated to 390° F. (199° C.), proving that it is held to the sulphate of copper by a more powerful chemical attraction. On this account it is spoken of as *water of constitution*, and, in order that the formula of the salt may exhibit the difference between the water of constitution and of crystallisation, it is usually written $CuSO_4.H_2O.4Aq$. (*Aqua*, water.)

(Definition.—*Water of crystallisation* of salts is that which is generally expelled at 212° F. (100° C.), and is connected with the form and colour of the crystals. *Water of constitution* is not generally expelled at 212° F., and is in more intimate connection with the chemical properties of the salt.)

Several of the so-called *sympathetic inks* employed for writings which are invisible until heated, depend upon the change of colour produced by loss of water of crystallisation. Characters written with a weak solution of cobalt chloride and allowed to dry, are very nearly invisible, since the pink colour of so small a quantity of the salt is scarcely noticed: but on warming the paper, the pink hydrated chloride of cobalt ($CoCl_2.6Aq$) loses water of crystallisation, and the blue chloride with one molecule of water is produced. On exposure to air this again absorbs water, and the writing fades away.

Some salts have so great a tendency to combine with water that they become moist or *deliquesce* when exposed to air. This *deliquescence* is exhibited in a marked degree by *calcium chloride* and its great attraction for water is turned to advantage in drying air and other gases by passing them through tubes filled with the salt.

Nearly all salts appear to combine with water at very low temperatures: such compounds, which are decomposed at temperatures above 0° C., have been termed *cryo-hydrates* (κρύος, frost). Common salt combines with ice to form the cryo-hydrate $NaCl.10Aq$, which remains liquid down to − 20° C. Hence arises the use of crushed ice and salt as a freezing mixture, for just as ice alone, in melting, lowers the temperature to 0° C., the melting-point of ice, so the compound of ice and NaCl, in melting lowers the temperature to about − 20° C., the melting-point of the cryo-hydrate.

41. Most bases are capable of combining with water to form hydrates, as exemplified in the slaking of lime. Anhydrous lime or quick-lime (CaO), when wetted with water, combines with it, evolving much heat, and crumbling to a loose bulky powder, which is hydrate of lime or slaked lime ($CaO.H_2O$). This affords an example of the second mode of attack referred to above; for some of the lime passes into solution when much water is used, but the original quick-lime cannot be recovered by merely evaporating the water. At a red heat, however, the water is expelled, and anhydrous lime remains.

42. Since several hydrates do not yield water when heated, the *hydrate of a metal* is defined as a compound formed by the exchange of a part of the hydrogen in water for a metal: thus potassium hydrate KOH is formed from water HOH by the exchange of H for K: calcium hydrate $Ca(OH)_2$ is formed from two molecules of water $(HOH)_2$ by the exchange of H_2 for (diad) calcium. The imaginary group OH, *hydroxyl*, would then be the *radicle of the hydrates*, which are often termed *hydroxides*.

43. *Water from natural sources.*—Pure water is not found in nature. Rain is the purest form of natural water, but contains certain gases which it collects from the atmosphere during its fall. As soon as it reaches the earth it begins to dissolve small portions of the various solid materials with which it comes in contact, and thus becomes charged with salts and other substances to an extent varying, of course, with the nature of the soils and rocks which it has touched, and attaining its highest point in sea water, which contains a larger proportion of saline matters than water from any other natural source.

If a quantity of rain, spring, river, or sea water be boiled in a flask furnished with a tube also filled with the water, and passing under a gas cylinder standing in a trough of the same water (Fig. 44), it will be found to give off a quantity of gas which was previously held in solution by the water, and is now set free because *gases are less soluble in hot than in cold water*. The quantity of this gas varies according to the source of the water, but always contains the gases existing in atmospheric air, viz., nitrogen, oxygen, and carbonic acid gas. One gallon of rain water will generally furnish about 4 cubic inches of nitrogen, 2 cubic inches of oxygen, and 1 cubic inch of carbonic acid gas. It is worthy of remark, that the nitrogen and oxygen have been dissolved by the water, not in the proportions in which they exist in the atmosphere, but in the proportions in which they ought to be dissolved, if it be true that they exist in the air in the condition of mere mechanical admixture. The oxygen thus carried down from the air by rain appears to be serviceable in maintaining the respiration of aquatic animals, and in conferring upon river waters a self-purifying power, by acting upon certain organic matters which would probably prove hurtful to animals, and converting them into harmless products of oxidation. In the cases of rivers contaminated with the sewage of towns, this action of the dissolved oxygen is probably of great importance. The carbonic acid dissolved in rain water also probably serves some useful purposes in the chemical economy of nature. (See *Carbonic Acid.*)

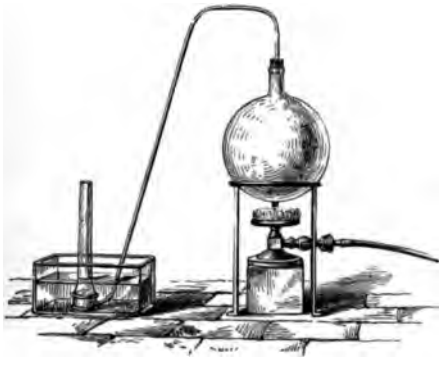


Fig. 44.

The *co-efficient of solubility* of a gas expresses the volume of gas absorbed by one volume of water. The numbers 0.02989 and 0.01478 respectively represent the

volumes of oxygen and nitrogen absorbed by one volume of water, when exposed to the action of either gas, in a pure state, at 59° F. (15° C.). When a mixture of gases is brought into contact with water, the proportions in which the gases are absorbed can be ascertained by multiplying the co-efficient of solubility of each gas by its proportion by volume in the mixture. Thus, when water is exposed to air, containing ⅕ volume of oxygen and ⅘ volume of nitrogen, the quantities dissolved by one volume of water are—

Oxygen . . . . . ⅕ × 0.02989 = 0.00597,
Nitrogen . . . . . ⅘ × 0.01478 = 0.01182;

or almost exactly two volumes of N to one volume of O.

44. The waters of wells, springs, and rivers, and especially those of the two first-named sources, differ very much from each other, according to the nature of the layers of rock or earth over or through which they have passed, and from which they dissolve a great variety of substances, some familiar to us in daily life, others only met with in chemical collections. Under the former head may be enumerated Glauber's salt (sodium sulphate), common salt (sodium chloride), Epsom salt (magnesium sulphate), gypsum (calcium sulphate), chalk (calcium carbonate), common magnesia (magnesium carbonate), carbonic acid, and silica.

Among the substances known only to the chemist may be mentioned sulphuretted hydrogen, potassium sulphate, potassium chloride, calcium chloride, magnesium chloride, phosphates, bromides and iodides of calcium and magnesium (rarely), aluminium sulphate, carbonate of iron (ferrous carbonate), and certain vegetable substances.*

The well waters of certain localities (as, for example, those of large towns) also frequently contain salts of nitric and nitrous acids, and of ammonia.

The waters of springs and rivers do not differ very materially from well waters as to the nature of the substances which they contain, though, in the case of river waters more particularly, the quantity of these substances is materially influenced by the conditions of rapid motion and exposure to air under which such waters are placed.

The palatable quality of a water is largely dependent upon the quantity of dissolved gas which it contains. Thus, a water which is agreeable for drinking will become insipid after it has been boiled and the dissolved air in this way expelled. The presence of dissolved solid matter in the water also influences its taste, preference being generally expressed for those waters which are not exceedingly poor in such solids; it is undesirable, however, that the quantity should exceed 35 grains per gallon (Thames water, as supplied to the metropolis, contains about 22 grains per gallon). A decision as to the wholesomeness of a water, or as to its fitness for feeding boilers, &c., can be given by the analyst alone; the considerations which influence his dictum are indicated in the following statements.

Household experience has established a classification of the waters from natural sources into *soft* and *hard* waters—a division which depends chiefly upon the manner in which they act upon soap. If a piece of soap be gently rubbed in soft water (rain water, for example) it speedily furnishes a froth or *lather*, and its cleansing powers can be readily brought into action; but if a hard water (spring water) be substituted for rain water, the soap must be rubbed for a much longer time before

* Although it is certainly known that the acids and bases capable of forming the salts here enumerated may be detected in spring and river waters, their exact distribution amongst each other is still a matter of uncertainty.

a lather can be produced, or its effect in cleansing rendered evident; a number of white curdy flakes also make their appearance in the hard water, which were not seen when soft water was used. The explanation of this difference is a purely chemical one.

Soap is formed by the combination of a fatty acid with an alkali; it is manufactured by boiling oil or fat with potash or soda, the former for soft, the latter for hard soaps. In the preparation of ordinary hard soap, the soda takes from the oil or fat two acids—*stearic* and *oleic* acid—which exist in abundance in most varieties of fat, and unites with them to form soap, which in chemical language would be spoken of as a mixture of *stearate* and *oleate of sodium*.

If soap be rubbed in soft water until a little of it has dissolved, and some Epsom salts (magnesium sulphate) be dissolved in water, and poured into the soap water, curdy flakes will be produced, as when soap is rubbed in hard water, and the soap water will lose its property of frothing when stirred; the magnesium sulphate has decomposed the soap, forming sodium sulphate, which remains dissolved in the water, and insoluble curdy flakes, which consist of stearate and oleate of magnesium.

Similar to the effect of the magnesium sulphate is that of hard waters; their hardness is attributable to the presence of the different salts of calcium and magnesium, all of which decompose the soap in the manner exemplified above; the peculiar properties of the soap in forming a lather and dissolving grease can therefore be manifested only when a sufficient quantity has been employed to decompose the whole of the salts of calcium and magnesium contained in the quantity of water operated on, and thus a considerable amount of soap must be rendered useless when hard water is employed.

On examining the interior of a kettle in which spring, well, or river water has been boiled, it will be found to be coated more or less thickly with a *fur* or incrustation, generally of a brown colour, and the harder the water the more speedily will this incrustation be deposited. A chemical examination shows this deposit to consist chiefly of calcium carbonate (chalk) in the form of minute crystals, which may be discovered by the microscope; it usually contains, in addition, some magnesium carbonate, calcium sulphate, and small quantities of oxide of iron (rust) and vegetable matter, the last two substances imparting its brown colour. In order to explain the formation of this deposit, it is necessary to become acquainted with the particular condition in which the calcium carbonate exists in natural waters; it is hardly dissolved to any perceptible extent by pure water, though it may be dissolved in considerable quantity by water containing carbonic acid. This statement, which is of great importance in connection with natural waters, may be verified in the following manner: A little slaked lime is well shaken up in a bottle of distilled or rain water, which is afterwards set aside for an hour or two; as soon as that portion of the lime which has not been dissolved has subsided, the clear portion is carefully poured into a glass, and a little soda water (a solution of carbonic acid in water) is added to it; the first addition of the carbonic acid to the lime water causes a milkiness, due to the formation of minute particles of calcium carbonate; this being insoluble in the water, separates from it, or *precipitates*, and impairs the transparency of the liquid; a further

addition of carbonic acid water renders the liquid again transparent, for the carbonic acid dissolves the calcium carbonate which has separated.

If this clear solution be introduced into a flask, and boiled over the spirit-lamp or gas-flame, it will again become turbid, for the free carbonic acid will be expelled by the heat, and the calcium carbonate will be deposited, not now, however, in so fine a powder as before, but in small, hard grains, which have a tendency to fix themselves firmly upon the sides of the flask, and, when examined by the microscope, are seen to consist of small crystals.

In a similar manner, when natural waters are boiled, the carbonic acid gas which they contain is expelled, and the carbonates of calcium, magnesium, and iron are precipitated, since they are insoluble in water which does not contain carbonic acid. But, by the ebullition of the water, a portion of it has been dissipated in vapour, and if there be much calcium sulphate present, the quantity of water left may not be sufficient to retain the whole of the salt in solution; calcium sulphate requires about 500 parts of cold water to dissolve it, and is nearly insoluble in water having a higher temperature than 212° F., as would be the case in boilers worked under pressure, so that it would readily be deposited. It contributes much to the formation of compact incrustations. Should the water contain much vegetable matter, this is often deposited in an insoluble condition, the whole eventually forming together a hard compact mass, composed of successive thin layers, on the bottom and sides of the vessel in which the water has been boiled. The "furring" of a kettle is objectionable, chiefly in consequence of its retarding the ebullition of the water, since the deposit is a very bad conductor of heat, and therefore impedes the transmission of heat from the fire to the water; hence the common practice of introducing a round stone or marble into the kettle, in order, by its perpetual rolling, to prevent the particles of calcium carbonate from forming a compact layer. In steam boilers, however, even more serious inconvenience than loss of time sometimes arises if this deposit be allowed to accumulate, and to form a thick layer of badly conducting material on the bottom of the boiler, since the latter is then liable to become red hot, and to collapse. But even though this calamity be escaped, the wear and tear of the boiler is very much increased in consequence of the formation of this deposit, since its hardness often renders it necessary to detach it with the hammer, much to the injury of the iron boiler-plates, which are also subject to increased oxidation and corrosion in consequence of the high temperature which the incrustation permits them to attain by preventing their contact with the water. Moreover, it is obvious that a greater expenditure of fuel is requisite in order to heat the water through such a non-conducting "boiler scale." Many propositions have been brought forward for the prevention of these incrustations; some substances have been used, of which the action appears to be purely mechanical, in preventing the aggregation of the deposited particles. Clay, sawdust, and other matters have been employed with this view; but the action of sal ammoniac (ammonium chloride), which has also been found efficacious, must be explained upon purely chemical principles. When this salt is boiled with calcium carbonate, mutual decomposition ensues, producing calcium chloride and

ammonium carbonate, of which salts the former is very soluble in water, while the latter passes off in vapour with the steam. The ammonium chloride, however, corrodes the metal of the boiler. Solutions of the caustic alkalies, of alkaline carbonates, arsenites, tannates, &c., are also occasionally employed to prevent the formation of incrustations in boilers, and probably act by precipitating calcium carbonate and other calcium compounds which act as *nuclei*, around which the *fur* collects as a loose deposit or *mud*.

The deposit formed in boilers fed with sea water consists chiefly of calcium sulphate and magnesium hydrate, the latter produced by the decomposition of the magnesium chloride present in sea water. As hydrochloric acid is another product of the decomposition of magnesium chloride solution, water containing any considerable quantity of this salt is liable to corrode the plates of a boiler.

The incrustations formed in cisterns and pipes by hard water are also produced by the carbonates of calcium and magnesium deposited in consequence of the escape of the free carbonic acid which held them in solution. Many interesting natural phenomena may be explained upon the same principle. The so-called *petrifying springs*, in many cases, owe their remarkable properties to the considerable quantity of calcium carbonate dissolved in carbonic acid which they contain; when any object, a basket, for example, is repeatedly exposed to the action of these waters, it becomes coated with a compact layer of the carbonate, and thus appears to have suffered conversion into limestone. The celebrated waters of the Sprudel at Carlsbad, of San-Filippo in Tuscany, and of Saint Allyre in Auvergne are the best instances of this kind.

The *stalactites* and *stalagmites*,* which are formed in many caverns or natural grottoes, afford beautiful examples of the gradual separation of calcium carbonate from water charged with carbonic acid. Each drop of water, as it trickles through the roof of the cavern, becomes surrounded with a shell of calcium carbonate, the length of which is prolonged by each drop, as it falls, till a stalactite is formed, varying in colour according to the nature of the substances which are separated from the water together with the carbonate (such as the oxides of iron and vegetable matter); and as each drop falls from the point of the stalactite upon the floor of the cavern, it deposits there another shell, which grows, like the upper one, but in the opposite direction, and forms a stalagmite, thus adorning the grotto with conical pillars of calcium carbonate, sometimes, as in the case of the *oriental alabaster*, variegated with red and yellow, and applicable to ornamental purposes.

When water which has been boiled for some time is compared with unboiled water from the same source, it is found to have become much softer, and this can now be easily explained, for, a considerable portion of the salts of calcium and magnesium having separated from the water, the latter is not capable of decomposing so large a quantity of soap. The amount of hardness which is thus destroyed by boiling is generally spoken of as *temporary* hardness, to distinguish it from the *permanent* hardness due to the soluble salts of calcium and magnesium which still remain in the boiled water. It is customary with analytical chemists, in reporting upon the quality of natural waters, to express the hardness by a certain number of degrees which indicate the number of grains of chalk or calcium carbonate which would be dissolved in a gallon of water containing carbonic acid, in order to render its hardness equal to that of the water examined; that is, to render it capable of decomposing an equal quantity of soap. Thus, when a water is spoken of as having 16 degrees of hardness, it is implied that 16 grains of calcium carbonate dissolved in a gallon of water containing carbonic acid, would render that gallon of water capable of decomposing as much soap as a gallon of the water under consideration.

* From σταλάζω, *I drop*: στάλαγμα, *a drop*.

The utility of a water for household purposes must be estimated herefore, not merely according to the total number of degrees of ardness which it exhibits, but also by the proportion of that hardness vhich may be regarded as temporary; that is, which disappears when he water is boiled. Thus, the total hardness of the New River water mounts to nearly 15 degrees, that of the Grand Junction Company to 14 degrees, and yet these waters are quite applicable to household uses, ince their hardness is reduced by boiling to about 5 degrees. It has een ascertained that every degree of hardness in water gives rise to a vaste of about 10 grains of soap for every gallon of water employed, and ience the use of 100 gallons of Thames or New River water in washing vill be attended with the loss of about 2 lbs. of soap; this loss is educed, however, to about one-third when the temporary hardness has een destroyed by boiling. The addition of washing soda (sodium arbonate) removes the permanent hardness due to the presence of the ulphates of calcium and magnesium in the water, for both these salts re decomposed by the sodium carbonate which separates the calcium nd magnesium as insoluble carbonates, whilst sodium sulphate remains issolved in the water.* The household practice of boiling the water, nd adding a little washing soda, is therefore very efficacious in removing the hardness. *Clark's process* for softening waters depends upon the neutralisation of the free carbonic acid contained in the water by the addition of a certain quantity of lime; the calcium carbonate so produced separates together with the carbonates of calcium and magnesium, which were previously retained in solution by the free carbonic acid; this process, therefore, affects chiefly the temporary hardness; moreover, the earthy carbonates which are separated appear to remove from the water a portion of the organic matter which it contains, and thus effect a very important purification. The water under treatment is mixed, in large tanks, with a due proportion of lime or lime-water (the quantity necessary having been determined by preliminary experiment), and the mixture allowed to settle until perfectly clear, when it is drawn off into reservoirs.† A modern improvement in the process (*Porter-Clark process*) consists in separating the deposit by a remarkably expeditious filtration, which dispenses with much of the tank-space required by the original process.

Waters which are turbid from the presence of clay in a state of suspension, are sometimes purified by the addition of a small quantity of alum or of aluminium sulphate, when the alumina is precipitated by the calcium carbonate present in the water, and carries down with it mechanically the suspended clay, leaving the water clear.

The *organic matter* contained in water may be vegetable matter dissolved from the earth with which it has come in contact, or resulting from the decomposition of plants, or it may be animal matter derived either from the animalcules and fish naturally existing in it, or from the sewage of towns, and, in the case of well waters, from surface drainage.

It is believed upon good medical authority, that cholera, diarrhœa, and typhoid fever are propagated by certain micro-organisms called

* $CaSO_4$ + Na_2CO_3 = Na_2SO_4 + $CaCO_3$
Calcium sulphate. Sodium carbonate. Sodium sulphate. Calcium carbonate.

† Thames and New River water are softened, in this way, to 3.5°, or to a lower point than by an hour's boiling.

bacilli, which are present in the evacuations of persons suffering from those maladies, and are conveyed into water which is allowed to become contaminated by sewage.

On this account, much attention is paid, in the analysis of water intended for drinking, to the detection of organic matters containing nitrogen (so-called *albuminoid* matters) which would be conveyed into the water in sewage. The analytical operations necessary for this purpose require great care and skill, and the conclusions to be drawn from their results are by no means finally agreed upon among scientific chemists. Attempts are also made to determine the number of *bacteria* (including bacilli) present in the water, which is rejected if these are very numerous.

There are, however, certain simple tests, which may often determine whether it is worth while to undertake a more elaborate examination of the water.

1. Pour half a pint of the water into a wide-mouthed bottle or decanter, close it with the stopper or with the palm of the hand, and shake it violently up and down. If an offensive odour is then perceived, the water is probably contaminated by sewage gas, and possibly with other constituents from the same source.

2. Add to a little of the water a drop or two of dilute sulphuric acid, and enough potassium permanganate (*Condy's red fluid* or *ozonised water*) to tinge it of a faint rose colour; cover the vessel with a glass plate or a saucer. If the pink tinge be still visible after the lapse of a quarter of an hour, the water is probably wholesome.

3. Pour a little solution of silver nitrate (*lunar caustic*) into a carefully *cleaned glass*, and see that it remains transparent; then pour in some of the water; should a *strong* milkiness appear, which is not cleared up on adding a little diluted nitric acid, the water probably contains much sodium chloride, which is always found in sewage-water, but seldom in wholesome waters in any large quantity, unless near the sea coast.

To render an impure water fit to drink, a chemist would naturally recommend distillation, but in many cases this is impracticable, and the consumer may protect himself to a great extent by boiling the water (a high temperature being inimical to micro-organisms), or by filtering it through charcoal or *spongy* iron, or by applying Clark's process, or treating it with alum (p. 59).

45. One of the most important points to be taken into account in estimating the qualities of a water is its action upon lead, since this metal is unfortunately so generally employed for the storage and transmission of water, and cases frequently occur in which the health has been seriously injured by repeated small doses of compounds of lead taken in water which has been kept in a leaden cistern. If a piece of bright, freshly-scraped lead be exposed to the air, it speedily becomes tarnished from the formation of a thin film of the oxide of lead, produced by the action of the atmospheric oxygen; this oxide of lead is soluble in water to some extent, and hence, when lead is kept in contact with water, the oxygen which is dissolved in the latter acts upon the metal, and the oxide so produced is dissolved by the water; but fortunately, different waters act with very different degrees of rapidity upon the metal, according to the nature of the substances which they contain.

The film of oxide which forms upon the surface of the lead is insoluble, or nearly so, in water containing much sulphate or carbonate of calcium, so that hard waters may generally be kept without danger in leaden cisterns, but soft waters, and those which contain nitrites or nitrates, should not be drunk after contact with lead.

Nearly all waters which have been stored in leaden cisterns contain a trace of the metal, and since the action of this poison, in minute doses, upon the system is

ıl that the mischief is often referred to other causes, it is much to be hat lead should be discarded altogether for the construction of cisterns. *d.*)

ect lead in a water, fill a glass tumbler with it, place this on white paper, op or two of diluted nitric acid, and some hydrosulphuric acid ; a dark ıge will be seen on looking through the water from above.

ral waters, as they are popularly called, are simply spring waters ing so large a quantity of some ingredient as to have a decided al action. They are differently named according to the nature predominating constituent. Thus, a *chalybeate* water contains erable quantity of a salt of iron (usually ferrous carbonate dis- y free carbonic acid); an *acidulous* water is distinguished by a oportion of carbonic acid, and is well exemplified in the cele- Seltzer water; a *sulphureous* or *hepatic* water has the nauseous ue to the presence of sulphuretted hydrogen. The Harrogate eminently sulphureous. *Saline* waters are such as contain a ıantity of some salt; thus the saline springs of Cheltenham are common salt and sodium sulphate.

chalybeate waters, which are by no means uncommon, become when exposed to the air, and deposit a rusty sediment which of the ferric hydrate, formed by the action of the oxygen of the he carbonate. (See *Iron.*)

Sea water contains the same salts as are found in waters from ıtural sources, but is distinguished by the very large proportion ım chloride (common salt). A gallon of sea water contains about 2500 grains of saline matter, of which 1890 grains consist ıon salt. The circumstance that clothes wetted with sea water ecome perfectly dry is to be ascribed chiefly to the *magnesium* present in the water, which is distinguished by its tendency to e or become damp in moist air. There are two elements, and *iodine*, which are found combined with metals in appreciable in sea water, though they are of somewhat rare occurrence in aters derived from natural sources.

By *distillation* pure water may be obtained from most spring and ıters.

NITION.—*Distillation* is the conversion of a liquid into a vapour re-condensation into the liquid form in another vessel.)

; represents the ordinary form of still in common use, in which A is a oiler containing the water to be distilled ; B the *head* of the still, which at *b*, and is connected by the neck C with the *worm* D, a tin pipe coiled the tub E and issuing at F. The steam from the boiler, passing into the condensed to the liquid state, being cooled by the water in contact with ı; this water, becoming heated, passes off through the pipe G, being by cold water, which is allowed to enter through H. If 10 gallons of er be taken, 8½ may be distilled over, but the first half-gallon should be separately, as it contains ammonia and carbonic acid.

ı of apparatus for distillation of water and other liquids is shown in A is a stoppered *retort*, the neck of which fits into the tube of a *Liebig's* (B), which consists of a glass tube (C) fitted by means of corks into a per, or tinned iron tube D, into which a stream of cold water is passed nnel E, the heated water running out through the upper tube F. The nished by the condensation of the steam passes through the *quilled* , into the flask H. Heat is gradually applied to the retort by a ring gas-

special precautions are requisite in order to obtain absolutely

pure distilled water for refined experiments, but for ordinary purposes the common methods of distillation yield it in a sufficient pure condition.

The saline matters present in the water are of course left behind in the still or retort. Sea water is now frequently distilled on board ship

Fig. 45.

when fresh water is scarce. The vapid and disagreeable taste of distilled water, which is due to its having been deprived of the dissolved air during the distillation, is remedied by the use of *Normandy's still*, which provides for the restoration of the expelled air.

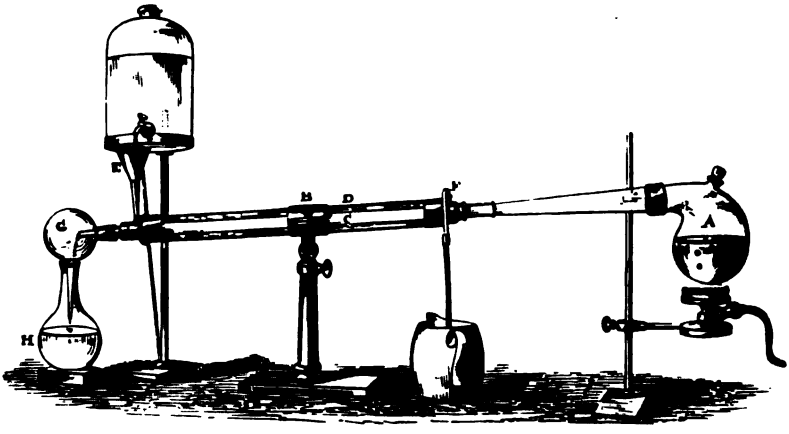


Fig. 46.—Distillation : Liebig's condenser.

48. The physical properties of water are too well known to require any detailed description. Its specific gravity in the liquid state = 1,

being taken as the standard to which the specific gravities of liquid and solid bodies are referred.

(DEFINITION.—The *specific gravity of a liquid or solid body* is its weight as compared with that of an equal volume of pure water at 60° F.—15.5° C.)

Water assumes the solid form, under ordinary circumstances, at 32° F. (0° C.), and may be obtained in six-sided prismatic crystals. Snow consists of beautiful stellate groupings of these crystals. Ice has the specific gravity 0.9184. In the act of freezing, water expands very considerably, so that 174 volumes of water at 60° F. become 184 volumes of ice. The breakage of vessels, splitting of rocks, &c., by the congelation of water are due to this expansion. Water passes off in vapour at all temperatures, the amount of water evolved in a given time of course increasing with the temperature. The boiling-point of water is 212° F. (100° C.). Its *absolute* boiling-point (p. 29) is 365° C.

(DEFINITION.—The *boiling-point* of a liquid is the constant temperature indicated by a thermometer, immersed in the vapour of the boiling liquid, in the presence of a coil of platinum wire, to facilitate disengagement of vapour, and at a pressure of 760 mm. Bar.)

At and above 212° F. at the ordinary atmospheric pressure (30 in. Bar.), water is an invisible vapour of specific gravity 0.625 (air = 1). One cubic inch of water at 60° F. becomes 1696 cubic inches of vapour at 212° F.

From the definition of molecular weight given on p. 47 it will be seen that if the specific gravity of a gas in relation to air be required, it may be obtained by multiplying half the molecular weight by 0.0695, which represents the specific gravity of hydrogen referred to air as the unit. Thus the specific gravity of steam (air = 1) is $9 \times 0.0695 = 0.625$.

49. **Peroxide of Hydrogen or Hydrogen Dioxide, H_2O_2** (oxygenated water). Minute quantities of this compound are found in snow and rain, but no other natural occurrence of it has been proved with certainty.*

To prepare hydrogen dioxide the barium dioxide referred to on p. 39 is powdered, suspended in water, and added gradually to water through which carbon dioxide is passing; the water is thus charged with hydrogen dioxide:

$$BaO_2 + H_2O + CO_2 = BaCO_3 + H_2O_2.$$

The barium carbonate ($BaCO_3$) is allowed to settle, and the clear solution of H_2O_2 poured off.

Pure hydrogen dioxide is made by first dissolving BaO_2 in the least possible quantity of dilute nitric acid and adding to the solution one of barium hydroxide (baryta water). The precipitate is $BaO_2.8H_2O$; it is washed by decantation and gradually added to dilute H_2SO_4, care being taken to leave the liquid *very slightly* acid †: $BaO_2 + H_2SO_4 = H_2O_2 + BaSO_4$. The precipitate is allowed to settle, and the clear liquid is evaporated either in a vacuum over oil of vitriol, or on the water-bath at a temperature below 75° C., until it contains about 50 per cent. of H_2O_2, when it is finally distilled under a pressure of 10–70 mm.; the water passes over first and then the pure dioxide. The operations of concentration and distillation require great care, and the solution first made should be free from salts of the heavy metals; for incautious heating of, the access of dust to, or the presence of such salts in, the concentrated dioxide renders it liable to explode by sudden decomposition into water and oxygen: $H_2O_2 = H_2O + O$. Even when preserved

* H_2O_2 is frequently produced when substances are oxidised by free oxygen in presence of water; thus it is invariably to be detected in water in which lead has been exposed to the air.

† If the H_2SO_4 were added to the $BaO_2.8H_2O$, instead of as recommended, the H_2O_2 would be decomposed by the remaining BaO_2 as fast as it was formed.

from adventitious matter the pure dioxide slowly decomposes, so that dangerous pressure due to accumulated oxygen may arise in any closed vessel containing it.

Pure hydrogen dioxide is a syrupy, colourless liquid of sp. gr. 1.5 and boiling at 69° C. under 26 mm. pressure. It is more soluble in ether than in water, so that the former extracts it from its solution in the latter. It oxidises many organic matters so rapidly that it sometimes ignites them. Its tendency to explode has been already mentioned.

When diluted with water, hydrogen dioxide is in no sense dangerous, although far from a stable substance. The commercial "10 volume" hydrogen peroxide contains about 3 per cent. of H_2O_2, and yields, from 1 volume of the solution, 10 volumes of oxygen when decomposed. It may be preserved for a considerable time if it contain a small proportion of acid; alkali has the opposite effect, and if the solution is neutral, it takes up alkali from the glass bottle and is decomposed thereby.

A remarkable feature of hydrogen dioxide is the ease with which it decomposes into water and oxygen, with evolution of heat, by mere contact with many substances which are themselves unchanged by the dioxide.* Thus, finely divided gold, platinum, and silver, which have no direct attraction for oxygen, cause this evolution of oxygen. Manganese dioxide also decomposes the H_2O_2 in a solution without undergoing any apparent change; but if an acid be present the MnO_2 will be reduced to MnO and will dissolve as a manganous salt, a fact which is somewhat surprising, seeing that the H_2O_2 is so ready to part with its oxygen. There are, however, a number of reactions in which hydrogen dioxide acts as a reducing agent. If some of the 3 per cent. solution be added to some silver oxide suspended in water, the brown colour of the oxide will pass into the black of finely divided silver and minute bubbles of oxygen will escape: $Ag_2O + H_2O_2 = Ag_2 + H_2O + O$. By adding ammonia very carefully to silver nitrate solution until the precipitate formed at first is only just re-dissolved, and then adding some H_2O_2 and heating, the silver will be deposited in its lustrous form, convincing the experimenter that it is indeed in the metallic state.

Another reducing action of H_2O_2 is its effect on an acid solution of potassium permanganate ($K_2Mn_2O_8$), the pink colour of which it rapidly discharges, with evolution of oxygen: $K_2Mn_2O_8 + 3H_2SO_4 + 5H_2O_2 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$. Here O_5 from the dioxide have united with O_5 from the permanganate.

Notwithstanding its behaviour in the foregoing changes as a reducing agent, a compound so ready to part with its oxygen, as is hydrogen dioxide, will, of course, act as an oxidising agent. If some black lead sulphide is treated with hydrogen dioxide it is rapidly oxidised to the white lead sulphate, $PbS + 4H_2O_2 = PbSO_4 = 4H_2O$. It is to be noted that in many cases the oxidising effect of the dioxide is much accelerated by the presence of a small quantity of a reducing agent; thus a mixture of indigo solution and the dioxide is at once decolourised (by oxidation of the indigo) on addition of a drop of ferrous sulphate solution.

A very striking reaction of hydrogen dioxide is that with chromic acid. If a solution of H_2O_2 be added to a weak solution of potassium dichromate acidified with sulphuric acid, the beautiful blue colour of perchromic acid appears; $K_2Cr_2O_7 + H_2SO_4 + H_2O_2 = K_2SO_4 + H_2O + H_2Cr_2O_8$.† After a few minutes, the blue colour changes to a very pale green, the perchromic acid being decomposed by the sulphuric acid, yielding the green chromium sulphate, and free oxygen, which adheres in bubbles to the side of the vessel, $H_2Cr_2O_8 + 3H_2SO_4 = Cr_2(SO_4)_3 + 4H_2O + O_4$. If the blue solution be shaken with a little ether, which dissolves the perchromic acid and rises with it to the surface where it forms a blue layer, the colour is much more lasting, and very minute quantities of hydrogen dioxide may thus be detected. Still more delicate tests for hydrogen dioxide are the production of a yellow colour with titanic acid, and a yellowish precipitate with uranium salts.

The decomposition of H_2O_2 into H_2O and O is attended by evolution of heat, amounting to 23,000 gram-units of heat for each gram-molecule of H_2O_2. When H_2 and O combine to form H_2O, 69,000 units of heat are evolved; hence, when H_2O is decomposed, 69,000 units must be absorbed, so that we have, in the formation of water, $H_2 + O = H_2O + 69{,}000$ heat-units. But since the decomposition of H_2O_2 into H_2O and O evolves 23,000 units, its formation from H_2O and O would

* Such inexplicable changes as this are sometimes included under the general denomination of *catalysis*, or decomposition by contact or by *catalytic action*.

† It is by no means certain that this formula represents the composition of the blue compound.

absorb the same quantity, and we should have $H_2O + O = H_2O_2 - 23{,}000$ units. From the two equations we get $H_2 + O_2 = H_2O_2 + 69{,}000 - 23{,}000$ or $H_2 + O_2 = H_2O_2 + 46{,}000$ heat-units. Now, by the laws of thermo-chemistry, *every chemical change tends to produce that body in the formation of which most heat is liberated;* hence water, and not hydrogen dioxide, is the general result of chemical changes in which H and O are concerned.

The uses of hydrogen peroxide are chiefly as an oxidising agent. Thus it is applied for bleaching materials which are too tender to be subjected to the drastic action of bleaching powder. A like effect is produced on dark hair, which becomes yellow on treatment with hair-wash containing this reagent. Photography, ivory-bleaching, and cleaning old pictures afford other outlets for hydrogen peroxide.

50. **Ozone.**—This is the name given to a modified form of oxygen, of the true nature of which there is still some doubt, as it has never been obtained unmixed with ordinary oxygen, but it appears to be formed by the union of 3 atoms of oxygen (occupying 3 volumes), to produce a molecule of ozone (occupying 2 volumes). Just as hydrogen dioxide (H_2O_2) may be regarded as formed by the combination of a molecule of water (H_2O) with an atom of oxygen, so ozone may be viewed as a combination of a molecule of oxygen (O_2) with an atom of oxygen. It would then be half as heavy again as ordinary oxygen, and experiment has shown that its rate of diffusion is in accordance with this view.

It derives its name from its peculiar odour (ὄζειν, *to smell*), which is often perceived in the air of the sea or of the open country, and in linen which has been dried in country air. According to Hartley, 1 volume of ozone in 2½ million volumes of air may be perceived by the smell. Oxygen appears to be capable of assuming this *ozonised* condition under various circumstances, the principal of which are, the passage of silent electric discharges,* and the contact with substances (such as phosphorus) undergoing slow oxidation in the presence of water. A portion † of the oxygen obtained in the decomposition of water by the galvanic current also exists in the ozonised condition, as may be perceived by its odour.

The use of an induction-tube (Fig. 47) affords the readiest method of demonstrating the characteristic properties of ozone.

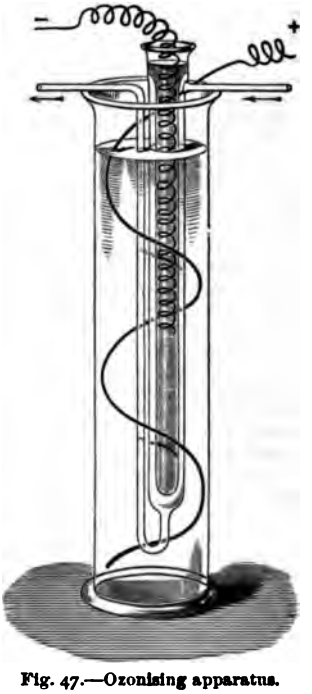


Fig. 47.—Ozonising apparatus.

The construction of the apparatus will be readily understood from the figure. The outside cylinder and the innermost tube are filled with dilute sulphuric acid, which serves the double purpose of conducting the electricity and keeping down the temperature of the oxygen or air. When the wires are connected with the poles of an induction-coil the two portions of dilute sulphuric acid are oppositely electrified, so that the space between the two liquids is submitted to the high pressure electrical discharge necessary for the resolution of the oxygen molecules into their atoms, and the recombination of these to form molecules of ozone. Through this space the air or oxygen (dried by passing through oil of vitriol) is passed in the direction of the arrows. The induction-tube must be made of thin glass, and the space between the inner and the outer tube must be as narrow as possible.

The ordinary chemical test for ozone is a damp mixture of starch paste with potassium iodide. If this mixture be brushed over strips of white cartridge paper

* It is the odour of ozone which is perceived in working an ordinary electrical machine.

† Varying from a trace to 17 per cent., according to the electrical conditions.

these will remain unchanged in ordinary air; but when they are exposed to ozonised air (such as that which has passed through the induction-tube), they will immediately assume a blue colour. The ozone sets free the iodine from the KI, which has the specific property of imparting a blue colour to starch. Papers impregnated with manganese sulphate, lead acetate, or thallous oxide, become brown, in the first two cases from the formation of the peroxide of the metal and in the last case from the formation of thallic oxide, under the influence of ozone.

If the ozonised air be passed into a solution of indigo (*sulphindigotic acid* largely diluted) the blue colour will soon disappear, since the ozone oxidises the indigo, and gives rise to products which, in a diluted state, are nearly colourless. Ordinary oxygen is incapable of bleaching indigo in this manner. If the ozone is passed through a tube of vulcanised caoutchouc, this will soon be perforated by the corrosive effect of the ozone, whilst ordinary oxygen would be without effect upon it. If ozonised air be passed into a flask with a little mercury at the bottom, the surface of the mercury will soon become tarnished by the formation of oxide, and when the mercury is shaken round the flask it will adhere to the sides, which is not the case with pure mercury. It is stated that if both the mercury and the ozone be dry, the gas will be converted into oxygen, but the mercury will not be oxidised.

When ozone is passed slowly through a glass tube heated in the centre by a spirit-lamp, it loses its power of affecting the iodised starch-paper, the ozone having been re-converted into ordinary oxygen under the influence of heat: $2(OO_2) = 3(O_2)$. A temperature of 250° C. is sufficient to effect this change. A given volume of oxygen diminishes when a portion of it is converted into ozone by the silent electric discharge, and it regains its original volume when the ozone is re-converted by heat. The conversion of oxygen into ozone is attended by absorption of heat; $3O_2 = 2O_3 - 59{,}200$ units.

When a given quantity of oxygen is *electrised*, or subjected to the action of surfaces charged with opposite electricities, as in the induction tube, only one-fifth, at most, is converted into ozone; but if the ozone be now removed by some substance which absorbs it, a fresh quantity of the oxygen may be ozonised.*

The facts that ozone can be produced in pure oxygen and that its formation is accompanied by a contraction in volume, lead to the conclusion that ozone is a condensed form of oxygen. When the ozonised oxygen has been heated it is found to have expanded to exactly the same volume which the pure oxygen occupied, and to no longer contain any ozone. By introducing turpentine into the ozonised gas all the ozone is absorbed, and a measurement of the contraction caused by this absorption reveals the fact that the volume which has disappeared is twice the volume of the contraction effected by ozonising the oxygen. Thus, if n c.c. of gas disappeared when the oxygen was ozonised, $2n$ c.c. will be absorbed by the turpentine. Therefore 3 vols. of the original oxygen must have become 2 vols. of ozone, and if the gas had been heated, instead of having been treated with turpentine, these 2 vols. of ozone would have expanded again to 3 vols. of oxygen. If one atom of oxygen be regarded as occupying one volume, then one molecule (2 atoms) must occupy 2 vols.; so that in producing ozone one molecule of oxygen has been combined with one atom of oxygen, forming a molecule of ozone, O_2O.

When a neutral solution of potassium iodide is introduced into ozonised oxygen, there is no contraction in volume, and yet all the ozone is destroyed; at the same time iodine is liberated from the potassium iodide. If the quantity of this iodine be determined, it is found to be as much as would (under other circumstances) be liberated by a volume of oxygen identical with the volume which disappeared when the oxygen was ozonised. The explanation of these observations is easy if the above view of the constitution of ozone be adopted; for the facts may be expressed by the equation—

$$OO_2(2 \text{ vols.}) + 2KI + HOH = 2KOH + I_2 + O_2 (2 \text{ vols.}),$$

showing that it is the third atom of oxygen in the molecule of ozone which has

* The proportion of ozone formed depends upon the intensity and frequency of the electric discharge, the pressure, and the temperature. The last-named influence is the greatest. According to the older researches (1880) 20 per cent. of the oxygen becomes ozone at $-25°$ C., 12 per cent. at 20° C., and 2 per cent. at 100° C.; more lately (1893) it has been stated that 5.2 per cent. at 20° C., and only 10.4 per cent., even at $-73°$ C., can be ozonised.

liberated the iodine. If the solution of potassium iodide be acidified (and thus converted virtually into a solution of hydriodic acid), twice as much iodine will be liberated and the volume of the ozone will be reduced to one-half:

$$OO_2 \text{ (2 vols.)} + 4HI = 2H_2O + I_4 + O \text{ (1 vol.)}.$$

By placing a freshly scraped stick of phosphorus (scraped under water to avoid inflammation) at the bottom of a quart bottle, with enough water to cover half of it, and loosely covering the bottle with a glass plate, enough ozone may be accumulated in a few minutes to be readily recognised by the odour and the iodised starch. The water at the bottom of the bottle is found to contain, besides the phosphorus and phosphoric acids, formed by the slow oxidation of the phosphorus, some hydrogen dioxide, whence it has been supposed that the formation of ozone is due to the decomposition of a molecule of oxygen into electro-negative oxygen, which combines with another molecule of oxygen to form ozone, and electro-positive oxygen, which combines with a molecule of water to form hydrogen dioxide. Thus,

$$\overset{-+}{O_2} + \overset{+\ \ -}{OO} + H_2O = H_2OO + O_2O.$$

This view is supported by the circumstance that hydrogen dioxide appears to be produced in every case where ozone is formed in the presence of water.

When ozonised oxygen is shaken with hydrogen dioxide, the above equation is reversed, water and ordinary oxygen being formed.*

Impure ether and essential oils, such as turpentine, slowly absorb oxygen (and perhaps ozone) from the air. There are thus produced organic peroxides which yield hydrogen dioxide in contact with water, so that old samples of these compounds exhibit the reactions of hydrogen dioxide. A solution of hydrogen dioxide in ether (ozonic ether) has been used as a test for blood stains.

Contact with blood decomposes hydrogen dioxide, and the oxygen which is liberated is capable of blueing guaiacum resin. Accordingly, if a blood-stain be moistened with tincture of guaiacum (a solution of the resin in spirit of wine), and afterwards with the ozonic ether, it acquires an intense blue colour, which may be detected, even on a coloured fabric, by pressing a piece of white blotting-paper upon it.

Ozone has attracted much notice, because a minute proportion of the oxygen in the atmosphere appears sometimes to be present in this form, and its active properties have naturally led to the belief that it must exercise some influence upon the sanitary condition of the air. This idea is encouraged by the circumstance that no indications of ozone can be perceived in crowded cities, where there are so many oxidisable substances to consume the active oxygen, whilst the air in the open country and at the seaside does give evidence of its presence. Some chemists assert that their experiments have demonstrated the very important fact that a portion of the oxygen developed by growing plants is in the ozonised form, but the evidence on the subject is conflicting. Houzean fixes the maximum proportion of ozone at $\frac{1}{700000}$th of the volume of air. The proportion is highest in May and June, lowest in December and January.

Ozonised oxygen exhibits a sky-blue colour when viewed along a column of one metre in length. The blue colour becomes very deep under a pressure of several atmospheres. It has been suggested that the blue colour of the sky is due to our regarding it through the ozonised atmosphere. By passing ozonised oxygen through a tube immersed in liquid oxygen which is evaporating, the ozone is condensed to a blue liquid boiling at – 106° C. and yielding a violently explosive blue gas. Ozone is slightly soluble in water; 100 vols. water dissolve 0.83 vols. ozone (at 1° C.).

In want of stability ozone resembles hydrogen dioxide; contact with manganese dioxide converts it into ordinary oxygen. Even shaking with powdered glass will de-ozonise the ozonised oxygen. When kept for some days, all the ozone is gradually re-converted into oxygen.

ATMOSPHERIC AIR.

51. Atmospheric air consists chiefly of a mixture of nitrogen and oxygen, roughly in the proportion of 4 vols. N : 1 vol. O. There are

* The oxygen obtained by the action of warm sulphuric acid on barium dioxide, or on crystallised potassium permanganate, resembles ozone in its odour and action on the iodised starch paper.

also present a small proportion of argon, and very small proportions of carbonic acid gas (carbon dioxide) and ammonia. Vapour of water is, of course, always present in the atmosphere in varying proportions. Since the atmosphere is the receptacle for all gaseous emanations, other substances may be discovered in it by very minute analysis, but in proportions too small to have any perceptible influence upon its properties. Thus marsh-gas or light carburetted hydrogen, sulphuretted hydrogen, and sulphurous acid gas, can often be traced in it, the last especially in or near towns.

Although the proportion of oxygen in the air at a given spot may be much diminished, and that of carbonic acid gas increased, by processes of oxidation (such as respiration and combustion) at that place, the operation of wind and of diffusion so rapidly mixes the altered air with the immensely greater general mass of the atmosphere, that the variations in the composition of air in different places are very slight. Thus it has been found that the proportion of oxygen in the air in the centre of Manchester was, at most, only 0.2 per cent. below the average.

Composition of dry air by volume and by weight.

	Volume.	Weight.
Nitrogen	78.40 per cent.	75.95 per cent.
Oxygen	20.94 ,,	23.10 ,,
Argon	0.63 ,,	0.90 ,,
Carbon dioxide	0.03 ,,	0.05 ,,

The proportion of aqueous vapour may be stated, on the average, as 1.4 per cent. by volume, or 0.87 per cent. by weight of the air. The total weight of atmospheric air surrounding the globe exceedes 300,000 million tons. A litre of dry air at 0° C. and 760 mm. weighs 1.293 grams.

The exact volumetric analysis of air has been already given (p. 44).

The proportion of oxygen to nitrogen in air may be exhibited by suspending a stick of phosphorus upon a wire stand (A, Fig. 48) in a measured volume of air confined over water. The cylinder (B) should have been previously divided into five equal spaces, by measuring water into it, and marking each space by a

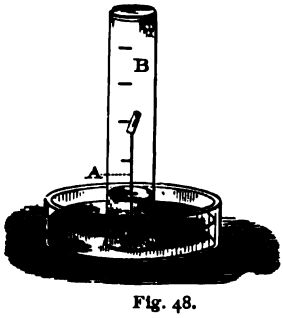


Fig. 48.

Fig. 49.

thin line of Brunswick black, After a few hours, the phosphorus will have combined with the whole of the oxygen to form phosphorous and phosphoric acids, which are absorbed by the water, leaving four of the spaces occupied by nitrogen.

The same result may be arrived at in a much shorter time by burning the phosphorus in the confined portion of air.

A fragment of phosphorus dried by careful pressure between blotting-paper, is placed upon a convenient stand (A, Fig. 49) and covered with a tall jar, having an opening at the top for the insertion of a well-fitting stopper (which should be greased with a little lard), and divided into seven parts of equal capacity. The jar should be placed over the stand in such a manner that the water may occupy the two lowest spaces into which the jar is divided. The stopper of the jar is furnished with a hook, to which a piece of brass chain (B) is attached, long enough to touch the phosphorus when the stopper is inserted. The end of this chain is heated, and the stopper tightly fixed in its place. On allowing the hot chain to touch the phosphorus, the latter bursts into vivid combustion, filling the jar with thick white fumes, and covering its sides for a few moments with white flakes of phosphoric anhydride. At the commencement of the experiment, the water in the jar will be depressed, in consequence of the expansion of the air due to the heat produced in the burning of phosphorus, but presently, when the combustion begins to decline, the water rises, and continues to do so until it has ascended to the line (C), so as to occupy the place of one-fifth of the air employed in the experiment. The phosphorus will then have ceased to burn, the white flakes upon the sides of the jar will have acquired the appearance of drops of moisture, and the fumes will have gradually disappeared, until, in the course of half an hour, the air remaining in the jar will be as clear and transparent as before, the whole of the phosphoric anhydride having been absorbed by the water. The jar should now be sunk in water, so that the latter may attain to the same level without as within the jar. On removing the stopper, it will be found that the nitrogen in the jar will no longer support the combustion of a taper.

In the rigidly accurate determination of the proportion of oxygen to nitrogen and argon in the air, it is of course necessary to guard against any error arising from the presence of the water, carbonic acid gas, and ammonia.* With this view,

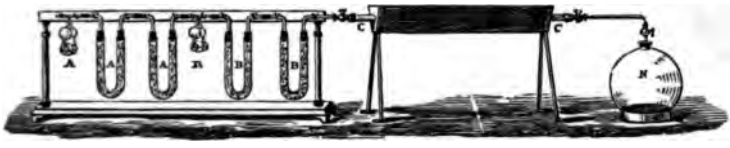


Fig. 50.—Exact analysis of air.

Dumas and Boussingault, to whom we are originally indebted for our exact knowledge of the composition of the air, caused it to pass through a series of tubes (A, Fig. 50) containing potash, in order to remove the carbonic acid gas, then through a second series (B) containing sulphuric acid, to absorb the ammonia and water; the purified air then passed through a glass tube (C) filled with bright copper heated to redness in a charcoal furnace, which removed the whole of the oxygen, whilst the nitrogen passed into the large globe (N).

Both the tube (containing the copper) and the globe were carefully exhausted of air and accurately weighed before the experiment; on connecting the globe and the tube with the purifying apparatus, and slowly opening the stop-cocks, the pressure of the external air caused it to flow through the series of tubes into the globe destined to receive the nitrogen. When a considerable quantity of air had passed in, the stop-cocks were again closed, and after cooling, the weight of the globe was accurately determined. The difference between this weight and that of the empty globe, before the experiment, gave the weight of the nitrogen which had entered the globe; but this did not represent the whole of the nitrogen contained in the analysed air, for the tube containing the copper had, of course, remained full of nitrogen at the close of the experiment. This tube, having been weighed, was attached to the air-pump, the nitrogen exhausted from it, and the tube again weighed; the difference between the two weighings furnished the

* It would be satisfactory, of course, to deprive the air of its argon also, in making this experiment, and thus arrive at the true proportion of nitrogen to oxygen; no method is known, however, for removing argon from a gas. It must be remembered that this gas has only recently been discovered, and Dumas and Boussingault estimated it with the nitrogen, thus making the proportion of this constituent too high.

weight of the nitrogen remaining in the tube, and was added to the weight of that received in the globe. The oxygen was represented by the increase of the weight of the exhausted tube containing the copper, which was partially converted into CuO by combining with the oxygen of the air passed through it.

52. **The nitrogen remaining (together with the argon) after the removal of the oxygen from air in the above experiments was so called on account of its presence in nitre (saltpetre, KNO_3). In physical properties it resembles oxygen, but is somewhat lighter than that gas, its specific gravity being 0.967.**

This difference in the specific gravities of the two gases is well exhibited by the arrangement shown in Fig. 51. A jar of oxygen (*O*) is closed with a glass plate, and placed upon the table. A jar of nitrogen (*N*), also closed with a glass plate, is placed over it, so that the two gases may come in contact when the glass plates are removed. The nitrogen floats for some seconds above the oxygen, and if a lighted taper be quickly introduced through the neck of the upper jar, it will be extinguished in passing through the nitrogen, and will be rekindled brilliantly when it reaches the oxygen in the lower jar.

Fig. 51.

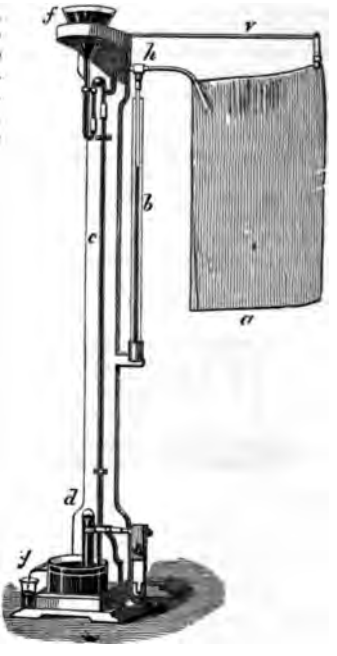


Fig. 52.—Sprengel's pump. Dialysis of air.

It might at first sight appear surprising that oxygen and nitrogen, though of different specific gravities, should exist in uniform proportions in all parts of the atmosphere, unless in a state of chemical combination; but an acquaintance with the property of diffusion (p. 25) possessed by gases, teaches us that *gases mix with each other in opposition to gravitation, and when mixed always remain so.*

It was shown by Graham that a partial separation of the nitrogen and oxygen in air may be effected, on the same principle as that of hydrogen and oxygen at page 28, by taking advantage of the difference in their rates of diffusion. He devised, however, a more convenient process, founded upon the *dialytic* (osmotic) passage of the gases through caoutchouc, which he ascribed to the absorption of the gas by the solid material upon one side, and its escape on the other.

A bag (*a*, Fig. 52) is made of a fabric composed of a layer of caoutchouc between two layers of silk, such as that employed for waterproof garments; a piece of carpet is placed inside the bag to keep the sides apart, and the edges of the bag

are made perfectly air-tight with solution of caoutchouc. To maintain a vacuum within the bag, it is supported by a rod *r*, and attached to *Sprengel's air-pump*, in which a stream of mercury, allowed to flow from a funnel (*f*) down a tube (*c*) six feet long, draws the air out of the bag, through a lateral tube (*h*), until all the air is exhausted, which is indicated by the barometer tube *b*, the lower end of which dips into a cistern of mercury. When the mercury in this tube stands at almost exactly the same height as the standard barometer, the exhaustion is complete. If a test-tube (*d*) filled with mercury be now inverted over the end of the long tube *c*, which is bent upwards for that purpose, the bubbles of air which are drawn through the sides of the vacuous bag, and carried down the long tube by the little pistons of liquid mercury as they fall, will pass up into the test-tube; when the latter is filled with the gas, its mouth is closed with the thumb, withdrawn from the mercury, and a match with a spark at the end inserted, when the spark will burst out into flame, showing that the specimen of air collected is much richer in oxygen than ordinary atmospheric air. The overflow tube *g* delivers the mercury which is to be returned to the funnel *f*.

The dialytic passage of oxygen through caoutchouc into a vacuum is twice as rapid as that of nitrogen, so that the air collected in the tube contains twice as much oxygen as the external air.

This osmotic passage of gases through solids is quite unconnected with diffusibility of the gases, and appears to depend rather upon the chemical nature of the gas and of the solid. It is thus connected with the *occlusion* of gases by solids. In consequence of this osmotic passage, tubes of iron or platinum, which are quite impermeable by hydrogen at the ordinary temperature, allow it to pass rapidly through their walls at high temperatures.

That air is simply a mechanical mixture of its component gases is amply proved by the circumstance that it possesses all the properties which would be predicted for a *mixture* of these gases in such proportions; whilst the essential feature of a *chemical compound* is, that its properties cannot be foreseen from those of its constituents. (See p. 6.)

The absence of active chemical properties is a very striking feature of nitrogen, and admirably adapts it for its function of diluting the oxygen in the atmosphere. This is even more true of the small proportion of argon in the air, for this gas appears to be devoid of all chemical properties.

The chemical relations of air to animals and plants will be more appropriately discussed hereafter. (See *Carbonic Acid*, *Ammonia*.)

In considering the composition of air, much attention has been directed of late years to the *dust* or minute particles of solid matter which, although much heavier than air, are suspended in it by the action of currents, and may always be detected by a beam from the sun or the electric lamp or the lime-light, which would be invisible along its track through *optically pure* air. Such dust has been found to contain iron, lime, silica, and other inorganic substances, besides organic matter.

The fine particles of mineral substances present in the dust are the probable cause of the crystallisation of supersaturated solutions of salts (p. 51) when exposed to air. The vegetable particles appear to contain minute seeds which germinate when deposited in certain liquid or moist solid substances, and give rise to *mould*, *mildew*, and fermentation. The animal particles are believed to contain the germs by the agency of which certain forms of disease are spread.

The dust of the air has also a considerable influence on the production of fogs. Air at the ordinary temperature (16° C.) is said to be "dry" when it contains less than 5 grams of water vapour per cubic metre (35.37 cubic feet), and "damp" when it contains more than 10 grams of water vapour in this volume, the sensation of dryness or

dampness having relation to the degree of rapidity with which the water excreted by the skin is able to evaporate. When damp air is chilled the water vapour is deposited from it in the form of fog, unless the air be optically pure, when no condensation of the water occurs. It would appear from this that the dust particles in the air form nuclei around which the aqueous vapour can precipitate, much as the crystals form around a particle in a super-saturated solution. The aggravation of a fog by smoke may perhaps be partly due to such a cause.

It has been shown that dust particles are not alone in causing precipitation of aqueous vapour, many gases which are free from suspended particles having a similar effect. Sulphur dioxide is an example; this gas is always present in London air, being a product of the combustion of coal containing iron pyrites; it is more abundant in foggy weather, but whether it is a cause of the fog or is merely retained thereby remains uncertain.

Liquid Air.—The simplest method of liquefying a gas is to cool it at atmospheric pressure to a temperature below that at which the liquid to be formed boils. Liquefaction then ensues just as steam condenses to water when cooled below 100° C. By increasing the pressure on a liquid, its boiling-point is raised, hence if a gas be compressed it requires less cooling to liquefy it, for the boiling-point of the liquid to be formed is higher. Thus it is generally economical to compress the gas, as well as cool it, and this was the method by which the majority of the gases were originally liquefied; it is illustrated in the chapter on *Ammonia*.

Oxygen, having a low critical temperature (p. 29), was not liquefied until a suitable means for obtaining such low temperature had been found. Advantage was taken of the latent heat of evaporation, that is, the heat absorbed when a liquid becomes a gas. An easily liquefied gas was evaporated around a vessel containing one more difficulty liquefied, which in its turn was evaporated around a still more difficulty liquefied gas, and so on. The liquids had successively lower boiling-points, so that the temperature descended by steps until at last the critical temperature of oxygen was attained, whereupon this gas could be liquefied by pressure.

The modern method of making liquid air depends on a disappearance of heat quite analogous to the latent heat of evaporation. If the ideal gas (p. 28) were allowed to expand without doing any work,* its temperature would remain unchanged. But when an imperfect gas expands it becomes a better gas, and in so doing absorbs heat for precisely the same reason that a liquid absorbs heat when it becomes a gas, but in much smaller degree. Now the higher the pressure or the lower the temperature of a gas, the higher is its degree of imperfection (p. 28), so that expansion from a higher pressure or at a low temperature absorbs more heat than when it occurs at a low pressure or at a high temperature.

The actual quantity of heat absorbed by expansion is much too small to lower the temperature of air to the liquefying-point, were it not for an ingenious method of storing up the cold produced by the expansion. In the Linde machine, for liquefying air, for example, the air which has been slightly cooled by expansion is used to cool that about to be

* Such as would be the case if it expanded into a vacuum, instead of against the pressure of the atmosphere.

expanded, and when this second quantity has expanded it cools a third quantity, and so on. The cumulative effect of this *regenerative cooling* is to lower the temperature of the air until it liquefies. Of course, to economise the cold, the same air is expanded and compressed alternately. From what was said above it will be seen that as the temperature of the air gets lower, each expansion entails a larger absorption of heat.

Fig. 53 represents an apparatus for applying the foregoing principles. Air compressed at some 200 atmospheres is admitted at *A* into a lengthy coil *B* of metal pipe, passing concentrically through a similarly coiled pipe *C*. The other end of the inner coil opens into a box *D* and is provided with a valve *E*. One end of the outer coil also opens into the box *D*, whilst the other end is connected with a compressing pump *T*. The coils and box are embedded in a packing of wool, not shown in the figure, contained in the casing *H*. To operate the apparatus the valve *E* is opened until the air issues into the box *D* at a reduced pressure of some 20 atmospheres. The expanded and consequently cooled air passes up the outer coil to pump *T*, which compresses it again to 200 atmospheres and forces it through

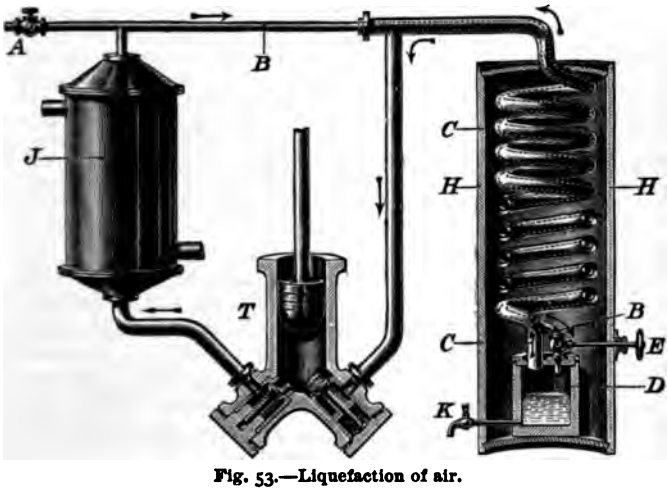


Fig. 53.—Liquefaction of air.

a coil of pipe round which water circulates in the cooler *J*. Here it is deprived of the heat imparted to it by the work of the pump, and is passed back to the inner coil to undergo the same cycle once more. It will be seen that as the air cooled by expansion passes around the inner coil, it cools the air about to be expanded, and that each portion of air issuing from the inner coil must be colder than that which preceded it. After a time this accumulated cold becomes sufficient to lower the temperature to − 193° C., whereupon liquid air collects in box *D* and may be drawn off through tap K. It is found more economical not to let the gas expand to atmospheric pressure, as the smaller amount of work necessary to pump air at 20 atmospheres pressure, and the increased cooling due to the work which the expanding gas has to do in moving the expanded gas at this pressure, more than balance the extra cooling which might be obtained by expansion to a lower pressure.

To preserve liquid air for more than a few moments it must be drawn off into a *vacuum vessel*, that is, a vessel surrounded by a shell enclosing a vacuous space around the walls of the vessel. The vacuum prevents passage of heat, and the effect is enhanced by silvering the surface of the shell so as to reflect heat rays falling upon it.

Since oxygen boils at a temperature some 10° C higher than that at which nitrogen boils, freshly made liquid air contains nearly 50 per

cent. by volume of oxygen. It is turbid from the presence of crystals of CO_2; after filtration through cotton wool it is a clear, mobile, bluish liquid, boiling at -193° C., freezing at a slightly lower temperature and of sp. gr. very nearly 1. The chief use of liquid air is as a source of oxygen which is obtained by fractionally distilling the liquid, so that the nitrogen boils away first.

Fractional distillation is the operation of separating mixed liquids by carefully raising their temperature so as to distil first that which has the lowest boiling-point.

The apparatus employed for separating oxygen and nitrogen in this manner is of the type shown in Fig. 54.

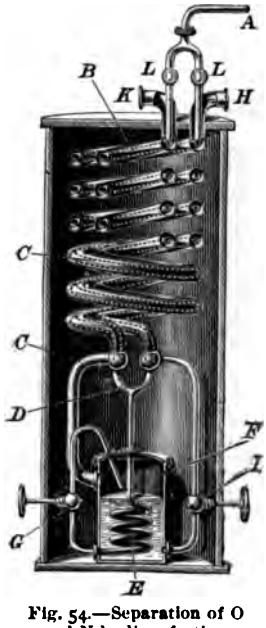


Fig. 54.—Separation of O and N by liquefaction.

Here the compressed air admitted at *A* passes through the inner pipes of two concentric coils *B* and *C*, the two currents uniting again at *D* to pass through a coil *E* situated in the receiver *F*. The valve *G* being opened, the air expands into the receiver and passes away through the outer pipe of the coil *C*. Presently, liquid air begins to collect in *F*, as in the apparatus already described, but its temperature is somewhat higher than in that case because of the air passing through the coil *E*. As a result nitrogen boils away from the liquid, and passing up the outer pipe of coil *B*, issues at *H*. By opening valve *I* the liquid oxygen in the receiver may be allowed to evaporate through the outer pipe of coil *B*, so as to be collected for use at the extremity *K*. The valves *L* are adjusted so that the proportion of hot gas passing through each coil may be in relation to the larger proportion of nitrogen than of oxygen passing away.

Attempts to liquefy hydrogen on the principle employed in liquefying air fail unless the hydrogen is first cooled to -205° C. by passing through a coil of metal pipe surrounded by liquid air boiling at reduced pressure. This may be ascribed to the fact that hydrogen is a much better gas than air, so that it is less cooled by expansion.*

One of the most remarkable of the many interesting experiments that can be performed with liquid air consists in absorbing it by a wad of cotton wool which has been mixed with finely divided charcoal and igniting the cotton; it burns like gun-cotton, and if fired by a small primer of mercuric fulminate it detonates with violence. It is said that this form of explosive has been used in blasting operations in excavating the Simplon tunnel.

NITROGEN.

N = 14 parts by weight = 1 vol.

53. Besides its presence in air, nitrogen is elsewhere found in nature as a constituent of saltpetre or potassium nitrate (KNO_3), and Chili saltpetre or sodium nitrate ($NaNO_3$). It also occurs as ammonia (NH_3) in the atmosphere and in the gaseous emanations from volcanoes. It is contained in the greater number of animal, and in many vegetable,

* Indeed, it appears that the cooling of the hydrogen by expansion is negligible until the temperature has fallen considerably, probably to about -80° C.

substances, and therefore has a most important share in the chemical phenomena of life.

Nitrogen is generally obtained by burning phosphorus in a portion of air confined over water (Fig. 55). The phosphorus is floated on the water in a small porcelain dish, kindled, and covered with a bell-jar. The nitrogen remains mixed with clouds of phosphoric anhydride (P_2O_5), which may be removed by allowing the gas to stand over water, 100 vols. of which dissolve only 1.4 vols. of nitrogen at the ordinary temperature.

Fig. 55.—Preparation of nitrogen.

When nitrogen is required in larger quantity, it is more conveniently prepared by passing air from a gas-holder, over metallic copper heated to redness in a tube. If the air be passed through solution of ammonia before passing over the heated copper, a short length of copper will suffice, since the oxide formed will be reduced by the ammonia; $3CuO + 2NH_3 = Cu_3 + 3H_2O + N_2$.

The nitrogen separated from air, however, always contains nearly 1 per cent. by volume of argon. To prepare pure nitrogen some compound of the element must be decomposed; thus an oxide of nitrogen may be passed over red hot copper. Or a solution of ammonium nitrite (or mixed solutions of potassium nitrite and ammonium chloride) may be boiled in a flask provided with a delivery tube; $NH_4NO_2 = 2H_2O + N_2$.

The remarkable chemical inactivity of free nitrogen has already been alluded to (p. 71). It has been seen, however, to be capable of combining directly with boron and silicon, and magnesium and titanium unite with it even more readily at a high temperature. Although it is so indifferent to oxygen at ordinary temperatures it unites with that element when a mixture of the two is subjected to the high temperature of electric sparks, forming oxides of nitrogen. Nitrogen is conspicuous among the elements for forming, with hydrogen, a powerful alkali (ammonia, NH_3), whilst the feeble chemical ties which hold it in combination with other elements, joined to its character of a permanent gas, render many of its compounds very unstable and explosive, as is the case with the so-called chloride and iodide of nitrogen, gun-cotton, the fulminates of silver and mercury, nitro-glycerine, &c.

The discovery of nitrogen was made in 1772 by Rutherford (Professor of Botany in the University of Edinburgh), who was led to it by the observation that respired air was still unfit to support life when all the carbonic acid had been absorbed from it by a caustic alkali. Hence the name *azote* (ἄ, priv., and ζωή, life), formally bestowed upon this gas.

Nitrogen becomes a colourless liquid at -194° C., the temperature at which it boils under atmospheric pressure. Its critical temperature is -146° C., and its critical pressure is 35 atmospheres. When rapidly evaporated a portion of the liquid nitrogen freezes to a colourless solid, melting at -214° C.

Nitrogen is the type of the trivalent elements (p. 11), its most stable compound with hydrogen being NH_3, ammonia.

Argon.

A = 39.6 parts by weight = 2 vols.

Rayleigh (1894) found that whereas 1 litre of nitrogen prepared from compounds of the element, such as from an oxide of nitrogen by passing it over red-hot copper, weighs 1.2505 gram, 1 litre of nitrogen prepared by depriving purified air of its oxygen weighs 1.2572 gram. Cavendish had long before recorded that when oxygen is added in small doses to atmospheric nitrogen through which electric sparks are passed and which is contained in a vessel also containing alkali to absorb the oxides of nitrogen produced, a small residue of gas is left which cannot be caused to combine with oxygen under the influence of the sparks. It has now been proved that Cavendish's residue is not obtainable when nitrogen other than that from the atmosphere is used, and that it is this residue which makes atmospheric nitrogen about $\frac{1}{2}$ per cent. heavier than other nitrogen, as observed by Rayleigh. The latter, in conjunction with Ramsay, examined the gas and concluded that it was an element so devoid of any tendency to combine with other elements, and therefore of chemical energy, that it might aptly be termed *argon* (*a*, *without*, *ἔργον*, *work*).

Argon is prepared by passing air first over caustic potash to absorb carbon dioxide, then through strong sulphuric acid to absorb aqueous vapour, and finally over red-hot magnesium or lithium which combines with the oxygen of the air to form magnesium or lithium oxide and with the nitrogen to form magnesium or lithium nitride.

As the combination of nitrogen with either metal does not occur rapidly, the passage of the gas through the red-hot tube containing the metal must be repeated several times before the argon is pure.

A modification of Cavendish's experiment also serves for obtaining argon. A large inverted flask (50 litres) is closed with a rubber cork through which pass five glass tubes. Through two of these are passed conducting wires terminating within the flask in platinum electrodes, and connected at their other ends with the poles of an apparatus (an electrical transformer supplied with 40 ampères at 30 volts), yielding electric current at very high pressure (6000 volts). A third tube serves for the introduction of a jet of caustic soda solution which plays against the side of the flask; a fourth tube serves to remove this solution as it runs down into the neck. Through the fifth tube, a mixture of 11 vols. oxygen and 9 vols. air is introduced continuously into the flask. When the transformer is set to work, an "electric flame" plays between the electrodes, and is probably an actual flame of burning nitrogen, for the latter rapidly disappears, being dissolved as oxides of nitrogen in the alkali.* About 20 litres of the gases may be combined per hour, and finally a mixture of argon and oxygen is obtained from which the latter may be absorbed by admitting pyrogallic acid.

The argon thus obtained amounts to 0.6 per cent. of the air. It is a colourless gas, without odour; it is 19.8 times as heavy as hydrogen so that its molecular weight is 39.6. It boils at $-186°$ C. and melts at $-189.5°$; its critical temperature is $-117.4°$ and its critical pressure 53 atmospheres; hence, at the ordinary temperature, it is far removed from the liquid state and obeys the gas laws well. 100 vols. of water dissolve 4.1 vols. of argon at 15° C., and the gas is found in the water from several mineral springs.

* Crookes has suggested the manufacture of nitrates in this manner from the atmosphere.

The most remarkable feature of argon is the fact that it has resisted all attempts to combine it with other elements; no compound of it is known. Hence its atomic weight has not been ascertained by the method outlined at p. 10; but it behaves physically as though its molecules were monatomic in which case its atomic weight is identical with its molecular weight.

Helium. He = 4 parts by weight = 2 vols.—When argon was discovered, search was made for it in other places than the atmosphere, and while submitting to spectrum analysis (*q.v.*) some gas obtained by heating the rare mineral *cleveite*, Ramsay (1895) detected a bright yellow line coinciding with that first detected (1868) in the spectrum of the luminous atmosphere which is seen surrounding the sun when he is eclipsed. The line had been ascribed to an element, provisionally named *helium*, but as no terrestrial matter had shown the same spectrum, it was concluded that the element was non-existent on the earth.

Ramsay's gas is no doubt the same matter as had been termed helium. It is obtainable from several other minerals, besides cleveite, by heating them, particularly such as contain uranium; the mineral is placed in a glass tube, which is then exhausted by a mercury pump (Fig. 70) and heated, the gas being collected by pumping it out of the tube. The helium is generally only a fraction of the total gas evolved, and must be separated from the other gases as argon is.

Helium is colourless, odourless, and exceedingly light, being only twice as heavy as hydrogen; its sp. gr. (air = 1) is 0.14. It is very slightly soluble in water, 100 vols. of water dissolving about 1.4 vols. at 15° C., and has resisted all attempts to liquefy it. It has been identified as accompanying argon in the water from the King's Well at Bath.

It is supposed that helium exists in minerals in a state of combination, but the gas not yet been caused to combine with any other element; hence its atomic weight is not chemically known. It behaves physically, however, like a monatomic gas, so that its atomic weight should be identical with its molecular weight, namely 4.

Krypton, Xenon, and Neon.—When a vessel containing argon, as it is prepared from the atmosphere, is cooled by immersion in liquid air, the gas liquefies, and on allowing the temperature to rise the first portion which boils off is a mixture of helium and another gas, *neon*, the vapour density of which is 20.3. The next gas to distil is argon, and the residue is a mixture of yet two other gases, *krypton*, of vapour density 40.5, and *xenon*, of vapour density 63.5. By several such fractional distillations the argon, krypton, and xenon are completely separated, and are recognised by their characteristic spectra. Helium and neon are separated by cooling them by liquid hydrogen, when the neon freezes. All these gases are supposed to have monatomic molecules. The amount of helium, krypton, neon, and xenon in the air is exceedingly small, about 0.0025 per cent. of the argon present.

Ammonia.

NH_3 = 17 parts by weight = 2 volumes.

54. Ammonia belongs to organic rather than to inorganic nature. It is generally a product of the decomposition of nitrogenous matter. Dead animal and vegetable matters yield it in *putrefaction*. Bones furnish it by *destructive distillation*; so does coal, the fossilised plant. Its compounds are found in beds of guano (the excrement of sea-fowl), and the most important of them, *sal ammoniac*, was first made in Egypt from the dung of camels. Its mineral sources are chiefly volcanic; ammonium sulphate is found in Tuscan boric acid, and occurs as *mascagnine* in the form of an efflorescence on recent lavas. It may be produced by the combination of nitrogen and hydrogen, induced by electric discharge, but its formation soon stops unless it is absorbed by an acid as fast as it is produced, because when 6 per cent. of the

mixed gases has become converted into ammonia the compound begins to be decomposed by the electric sparks.*

The proportion of ammonia existing in atmospheric air is so small that it is difficult to determine it with precision; it appears, however, not to exceed 5 milligrams in a cubic metre, for although ammonia is constantly sent forth into the air by the putrefaction of animal and vegetable substances containing nitrogen, it is soon absorbed by water, and even by earth and other porous solids. Rain water contains from 1 to 2 parts per million of ammonia. With the aid of certain micro-organisms in the soil, certain families of plants can utilise the uncombined nitrogen of the atmosphere as food for their growth, but for a large number of plants the chief supply of nitrogen is that contained in the ammonia, nitrates and nitrites contained in the air, the soil, and the water. During the life of an animal, it restores to the air the nitrogen which formed part of its wasted organs, mainly as urea and uric acid in the urine, the nitrogen of these being eventually converted into ammonia when the excretion undergoes putrefaction. Dead animal and vegetable matter, when putrefying, restores its nitrogen to the air, chiefly in the forms of ammonia and substances closely allied to it, but partly also, it is said, in the free state; when such matter is burnt all the nitrogen is liberated in an uncombined condition. Ammonia appears to be formed from atmospheric nitrogen by the growth of fungi (which evolve hydrogen) and by the decay of wood. Nitrogen is also slowly absorbed from air by sawdust mixed with lime and by glucose mixed with soda; the nitrogen being evolved as ammonia when these materials are afterwards heated with soda-lime.

The *liquor ammoniæ*, or solution of ammonia in water, which is so largely used in medicine and the arts, is obtained chiefly from the *ammoniacal liquor* resulting from the destructive distillation of coal for the manufacture of gas.† The ammoniacal liquor of the gasworks contains ammonia in combination with carbonic and hydrosulphuric acids. To recover the ammonia the liquor is heated with lime in a still; the ammonia and hydrosulphuric acid are thus expelled and are conducted into a covered tank containing sulphuric acid or hydrochloric acid, which absorbs the ammonia and allows the hydrosulphuric acid to escape through a pipe in the cover of the tank, to be burnt, or otherwise disposed of, in order that it may not cause a nuisance by its evil odour and poisonous properties. Ammonium sulphate or chloride (according to which acid has been used) crystallises from the acid in the tank. The former is sold as a manure; the latter is generally used for making pure ammonia. The crystals of *ammonium chloride* are moderately heated in an iron pan to deprive them of tar, and are finally purified by *sublimation*, that is, by converting them into vapour and allowing this vapour to condense again into the solid form. For this purpose the crystals are heated in a cylindrical iron vessel covered with an iron dome lined with fireclay. The ammonium chloride rises in vapour below a red heat, and condenses upon the dome in the form of the fibrous cake known in commerce as *sal ammoniac*.

* The heat evolved in the combination $N+H_3=NH_3$ is only 1195 gram units; hence it is not surprising that the reaction is difficult to realise.

† Considerable quantities of ammonia are now being recovered from the products of combustion obtained from *blast furnaces* (*q.v.*), in which, of course, it originates from the distillation of coal. The ovens in which coke is manufactured are also furnishing ammonia.

To obtain ammonia from this salt, an ounce of it is reduced to coarse powder, and rapidly mixed with 2 ounces of powdered quicklime. The mixture is gently heated in a dry Florence flask (Fig. 56), and the gas being little more than half as heavy as air (sp. gr. 0.59) may be collected in dry bottles by displacement of air, the bottles being allowed to rest upon a piece of tin plate which is perforated for the passage of the tube. To ascertain when the bottles are filled, a piece of red litmus-paper may be held at some little distance above the mouth, when it will at once acquire a blue colour if the ammonia escapes. The bottles should be closed with greased stoppers.

The action is explained by the following equation:

$$\underset{\text{Ammonium chloride.}}{2NH_4Cl} + \underset{\text{Lime.}}{CaO} = \underset{\text{Calcium chloride.}}{CaCl_2} + H_2O + \underset{\text{Ammonia.}}{2NH_3}.$$

The readiest method of obtaining gaseous ammonia for the study of its properties consists in gently heating the strongest *liquor ammoniæ* in a retort or flask

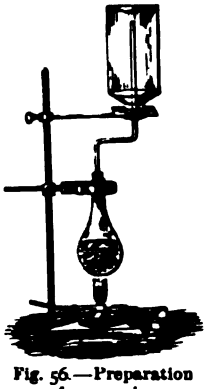


Fig. 56.—Preparation of ammonia.

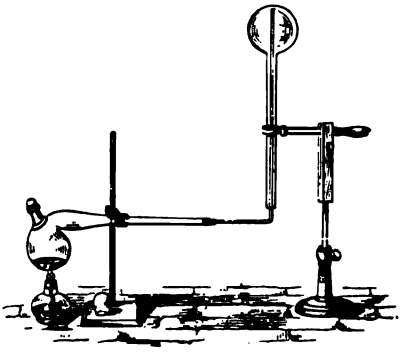


Fig. 57.

provided with a bent tube for collecting the gas by displacement (Fig. 57). The gas is evolved from the solution at a very low temperature, and may be collected unaccompanied by steam.

Ammonia is readily distinguished by its very characteristic smell, and its powerful alkaline action upon red litmus and turmeric papers. It is absorbed by water in greater proportion by volume than any other common gas, one volume of water absorbing more than 700 volumes of ammonia at the ordinary temperature, and becoming $1\frac{1}{2}$ volume of solution of ammonia. During the dissolution of the gas much more heat is evolved than corresponds with the heat of liquefaction of the gas; * this excess of heat can only be attributed to chemical combination; but no definite compound of ammonia with water has been obtained, and the gas gradually escapes on exposing the solution to the air. As is the case with all solutions of gases, the quantity of ammonia retained by the water is dependent upon the temperature and pressure; the escape of the gas from the solution is attended with great production of cold, much heat becoming latent in the conversion of the ammonia from the liquid to the gaseous state.

* Seventeen grams of ammonia evolve 20,300 gram-units of heat when dissolved in excess of water.

The rapid absorption of ammonia by water is well shown by filling a globular flask (Fig. 58) with the gas, keeping it with its mouth downwards in a small capsule of mercury which is placed in a large basin. If this basin be filled with water, it cannot come into contact with the ammonia until the mouth of the flask is raised out of the mercury, when the water will quickly enter and fill the flask. The water should be coloured with reddened litmus to exhibit the alkaline reaction of the ammonia.

That the amount of ammonia in solution varies with the pressure may be proved by filling a barometer tube, over 30 inches long, with mercury to within an inch of the top, filling it up with strong ammonia, closing the mouth of the tube, and inverting it with its mouth under mercury; on removing the finger the diminished pressure caused by the gravitation of the column of mercury in the tube will cause

Fig. 59.

Fig. 60.

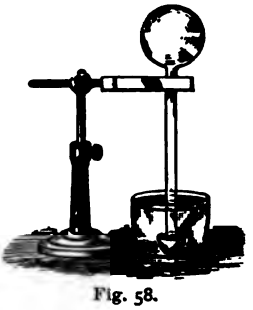


Fig. 58.

Fig. 61.

the solution of ammonia to boil, from the escape of a large quantity of the gas, which will rapidly depress the mercury. If the pressure be now increased by gradually depressing the tube in a tall cylinder of mercury (Fig. 59), the water will again absorb the ammoniacal gas.

To exhibit the easy expulsion of the ammoniacal gas from water by heat, a moderately thick glass tube, about 12 inches long and ½ inch in diameter, may be nearly filled with mercury, and then filled up with strong solution of ammonia; on closing it with the thumb, and inverting it into a vessel of mercury (Fig. 60), the solution will, of course, rise above the mercury to the closed end of the tube. By grasping this end of the tube in the hand, a considerable quantity of gas may be expelled, and the mercury will be depressed. If a little hot water be poured over the top of the tube, the latter will become filled with ammoniacal gas, which will be absorbed again by the water when the tube is allowed to cool, the mercury returning to fill the tube.

The solution of ammonia, which is an article of commerce, may be prepared by conducting the gas into water contained in a two-necked bottle, the second neck being connected with a tube passing into another bottle containing water, in which any escaping ammonia may be condensed. The strength of the solution is inferred from its specific gravity, which is lower in proportion as the quantity of ammonia in the solution is greater.

Thus, at 57° F. (14° C.), a solution of sp. gr. 0.8844 contains 36 parts by weight of ammonia in 100 parts of solution (*liquor ammoniæ fortissimus*); 0.9251, 20 per cent.; 0.9593, 10 per cent. (*British Pharmacopœia*). The specific gravity is ascertained by comparing the weights of equal volumes of water and of the solution at the same temperature. For this purpose a light stoppered bottle, or *picnometer*, is provided, capable of containing about two fluid ounces. This is thoroughly dried, and counterpoised in a balance by placing in the opposite pan a piece of lead, which may be cut down to the proper weight. The bottle is then filled with solution of ammonia, the temperature observed with a thermometer and recorded, the stopper inserted, and the bottle weighed. It is then well rinsed out, filled with distilled water, the temperature equalised with that of the ammonia by placing the bottle either in warm or cold water, and the weight ascertained as before. The specific gravity is obtained by dividing the weight of the solution of ammonia by that of the water. The *ammonia meter*, a form of *hydrometer* (Fig. 61), is a convenient instrument for rapidly ascertaining the specific gravity of liquids lighter than water. It consists of a hollow glass float with a long stem, weighted with a bulb containing shot or mercury, so that when placed in distilled water it may sink to 1000° of the scale marked on the stem, this number representing the specific gravity of water. When placed in a liquid lighter than water, it must, of course, sink lower in order to displace more liquid (since solids sink until they have displaced their own weight of liquid). By trying it in liquids of known specific gravities, the mark upon the scale to which it sinks may be made to indicate the specific gravity of the liquid. The ammonia meter generally has a scale so divided that it indicates at once the precentage weight of ammonia. In this country the specific gravity of a liquid is always supposed to be taken at 62° F. (16° C.).

The common name for solution of ammonia, *spirit of hart's horn*, is derived from the circumstance that it was originally obtained for medicinal purposes by distilling shavings of that material.

Ammonia is far removed from the ideal gas (p. 27); its critical temperature is about 130° C., so that it can be liquefied at the ordinary temperature, 6¼ atmospheres sufficing at 10° C. The liquid is colourless, has sp. gr. at 0° C. = 0.63 and boils at −33.5° C., so that the gas liquefies at this temperature under atmospheric pressure. It freezes to a white crystalline mass which melts at −78° C. The comparative ease with which the gas may be liquefied has led to its application in Carré's freezing apparatus (Fig. 61), in which the gas generated by heating a concentrated solution of ammonia in a strong iron boiler (A) is liquefied by its own pressure in an iron receiver (B) placed in cold water. When the boiler is taken off the fire and cooled in water, the liquefied ammonia evaporates very rapidly from the receiver back into the boiler, thereby producing so much

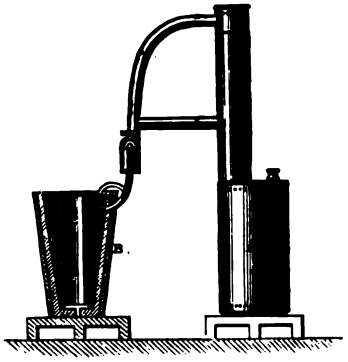


Fig. 62.—Carré's freezing apparatus.

cold * that a vessel of water (C) placed in spirit of wine contained in a cavity in the receiver, is at once congealed into ice.

To refrigerate large spaces by means of liquid NH_3, the gas is compressed by a pump into a coil immersed in a tank, and the liquid formed is allowed to evaporate through another coil also immersed in a tank, the gas returning to the suction side of the compression pump. Brine (which can be cooled considerably below 0° C. without freezing) is passed through the second tank where it is cooled by the evaporating NH_3, and then through pipes in the space to be cooled, then through the first tank, where it cools the compressed NH_3, and finally back into the second tank.

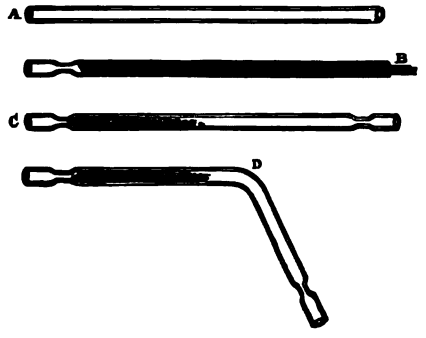


Fig. 63.

The liquefaction of ammonia is very easily effected by heating the ammoniated silver chloride ($AgCl.3NH_3$) in one limb of a sealed tube, the other limb of which is cooled in a freezing-mixture. A piece of stout glass tube (A, Fig. 137), about 12 inches long and ½ inch in diameter, is drawn out, at about an inch from one end, to a narrow neck. About 20 grams of silver chloride (dried at 400° F.) are introduced into the tube, so as to lie loosely in it. For this purpose a gutter of stiff paper (B) should be cut so as to slide loosely in the tube, the silver chloride placed upon it, and when it has been thrust into the tube (held horizontally) the latter should be turned upon its axis, so that the silver chloride may fall out of the paper, which may be then withdrawn. The tube is now drawn out to a narrow neck at about an inch from the other end, as in C, and afterwards carefully bent, as in D, care being taken that none of the chloride falls into the short limb of the tube, which should be about 4 inches long. The tube is then supported by a holder, so that the long limb may be horizontal, and is connected by a tube and

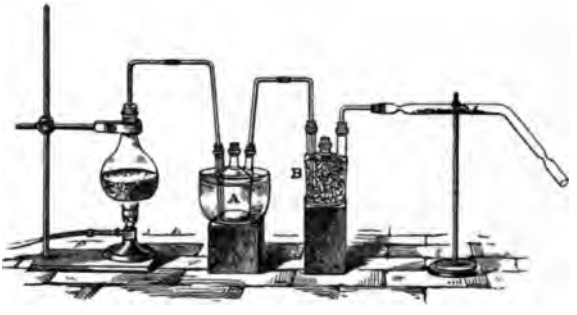


Fig. 64.

cork with an apparatus delivering dry NH_3, prepared by heating 80 grams of NH_4Cl with an equal weight of CaO in a flask, and passing the gas, first into an empty bottle (A, Fig. 64) standing in cold water, and afterwards through a bottle (B) filled with lumps of quicklime, to absorb all aqueous vapour. The long limb of the tube must be surrounded with filtering paper, which is kept wet with cold water. The current of ammonia should be continued at a moderate rate, until the tube and its contents no longer increase in weight, which will occupy about three hours—

* Seventeen grams of ammonia absorb 5661 gram units of heat in vaporising at −40° C. The specific heat of liquid ammonia between 0° and 20° C. is 1.02, being higher than that of water, a rare occurrence.

about 2.2 grams of NH_3 being absorbed. The longer limb is sealed by the blow-pipe flame whilst the gas is still passing, and then, as quickly as possible, the shorter limb, keeping that part of the tube which is occupied by the ammoniated silver chloride still surrounded by wet paper.

When the shorter limb of this tube is cooled (Fig. 65), in a mixture of ice and salt (or of 8 ounces of sodium sulphate and 4 measured ounces of common hydrochloric acid), whilst the longer limb is gently heated from end to end by waving a spirit-lamp beneath it, the NH_3 evolved by the heat from the ammoniated silver chloride, which partly fuses, condenses to a beautifully clear liquid in the cold limb. When this is withdrawn from the freezing-mixture, and the tube allowed to cool, the liquid ammonia boils and gradually disappears entirely, the gas being again absorbed by the silver chloride, so that the tube is ready to be used again.

Fig. 65.—Liquefaction of ammonia.

A small quantity of liquefied ammonia may be more conveniently obtained by means of a tube prepared as above, but containing about twelve inches of fragments of well-dried wood charcoal saturated with dry NH_3. The shorter limb of the tube should be drawn out to a long narrow point before sealing. This limb being immersed in the freezing-mixture, the other is placed in a long test-tube containing water, which is heated to boiling. The ammonia soon returns to the charcoal when the tube cools.

Liquefied ammonia dissolves potassium and sodium to a blue solution containing the compounds $KH_2N{\cdot}NH_3K$ and $NaH_2N{\cdot}NH_3Na$; iodine, sulphur, and phosphorus are also dissolved by it.

Ammonia is feebly combustible in atmospheric air, as may be seen by holding a taper just within the mouth of an inverted bottle of the gas, which burns with a peculiar livid flickering light around the flame, but will not continue to burn when the flame is removed, because the temperature produced by such a feeble combustion of the hydrogen in air is not high enough to continue the decomposition of the ammonia. During its combustion the hydrogen is converted into water, and the nitrogen set free. In oxygen, however, ammonia burns with a continuous flame.

This is very well shown by surrounding a tube delivering a stream of ammonia (obtained by heating strong solution of ammonia in a retort) with a much wider tube open at both ends (Fig. 66) through which oxygen is passed by holding a flexible tube from a gas-bag or gas-holder underneath it. On kindling the stream of ammonia it will give a steady flame of 10 to 12 inches long.

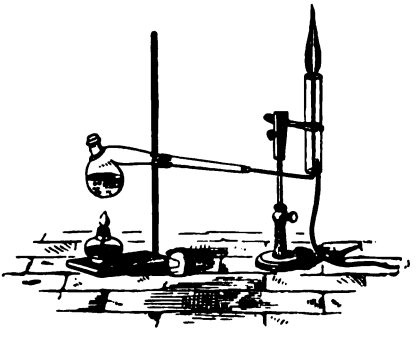


Fig. 66.

The elements of ammonia are easily separated from each other by passing the gas through a red-hot tube, or still more readily by exposing it to the action of the high temperature of the electric spark, when the volume of the gas rapidly increases until it is doubled, 2 volumes of ammonia being decomposed into 1 volume of nitrogen and 3 volumes of hydrogen, showing that the molecule of ammonia probably contains atoms of N and H in the proportion of 1 : 3.

For this experiment a measured volume of NH_3 is confined over mercury

(Fig. 67), in a tube through which platinum wires are sealed for the passage of the spark from an induction-coil. The volume of the gas is doubled in a few minutes, and if the tube be furnished with a stop-cock (A), the presence of free hydrogen may be shown by filling the open limb with mercury and kindling the gas as it issues from the jet. The decomposition ceases when only 3 per cent. of ammonia remains (p. 77).

Another method of demonstrating that ammonia is formed from 1 volume N and 3 volumes H takes advantage of the fact that when chlorine reacts with ammonia, the hydrogen of the latter combines with the former to make hydrogen chloride, HCl, which may readily be absorbed by water, leaving the nitrogen. The tube *A* (Fig. 68), graduated into three equal parts, is filled with chlorine. A strong solu-

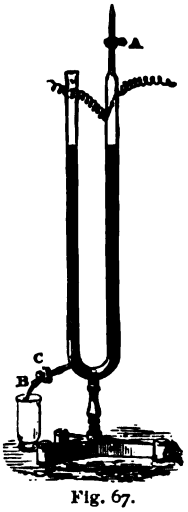


Fig. 67.

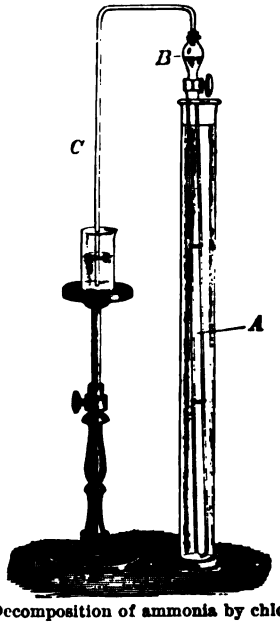


Fig. 68.—Decomposition of ammonia by chlorine.

tion of ammonia having been poured into the funnel *B*, the stop-cock is opened so that some of the NH_3 may enter the tube. A violent reaction ensues, and white fumes of ammonium chloride, NH_4Cl, are formed, due to the combination of the HCl produced with excess of NH_3. More ammonia is now admitted, and the tube is shaken. Owing to the fact that the NH_4Cl produced is a solid and dissolves in the water, the pressure in the tube is now below that of the atmosphere, so that when the bent tube *C*, dipping into water, is attached to the funnel and the stop-cock is opened, water rushes in to fill two-thirds of the tube. The remaining gas is found to be nitrogen.

Fig. 69.

As might be expected from its powerfully alkaline character, ammonia exhibits a strong attraction for acids, which it neutralises perfectly. If a bottle of ammonia gas, closed with a glass plate, be inverted over a similar bottle of hydrochloric acid gas, and the glass plates withdrawn (Fig. 69), the gases will combine, unless they be perfectly dry, (*cf.* p. 32), with disengagement of much heat, forming a white solid, ammonium chloride (NH_4Cl), in which the acid and alkali have neutralised each other. Again, if ammonia be added to diluted sulphuric acid, the latter will be entirely neutralised, and by evaporating the solution, crystals of ammonium sulphate, $(NH_4)_2SO_4$, may be obtained.

The substances thus produced by neutralising the acids with solution of ammonia bear a strong resemblance to the salts formed by neutralising the same acids with solutions of potash and soda, a circumstance which would encourage the idea that the solution of ammonia must contain an alkaline hydroxide (NH_4OH), similar to KOH or NaOH.

Berzelius was the first to make an experiment which appeared strongly to favour this view. The negative pole of a galvanic battery was placed in contact with mercury at the bottom of a vessel containing a strong solution of ammonia, in which the positive pole of the battery was immersed. Oxygen was disengaged at this pole, whilst the mercury in contact with the negative pole swelled to four or five times its original bulk, and became a soft solid mass, still preserving, however, its metallic appearance.* At a very low temperature the mass becomes dark grey and crystalline. So far, the result of the experiment resembles that obtained when potassium hydroxide is decomposed under similar circumstances, the oxygen separating at the positive pole, and the potassium at the negative, where it combines with the mercury. Beyond this, however, the analogy does not hold; for in the latter case the metallic potassium can be readily separated from the mercury, whilst in the former, all attempts to isolate the ammonium have failed, for the soft solid mass resolves itself, almost immediately after its preparation, into mercury, ammonia (NH_3), and hydrogen, one volume of the latter being separated for two volumes of ammonia. This would also tend to support the conclusion that a substance having the composition NH_3+H or NH_4 had united with the mercury; and since the latter is not known to unite with any non-metallic substance without losing its metallic appearance, it would be fair to conclude that the soft solid was really an amalgam of ammonium. However, the increase in the weight of the mercury is so slight, and the "amalgam," whether obtained by this or by other methods, is so unstable, that it would appear safer to attribute the swelling of the mercury to a physical change caused by the presence of the ammonia and hydrogen gases. This view is supported by the observation that when the amalgam is subjected to pressure its volume varies nearly in the inverse ratio of the pressure. It is difficult to believe that the solution of ammonia does really contain ammonium hydroxide ($NH_3+H_2O=NH_4OH$), when we find it evolving ammonia so easily, although at 0° C. the amount of ammonia dissolved approaches that required for this formula; but it is equally difficult, upon any other hypothesis, to explain the close resemblance between the salts obtained by neutralising acids with this solution and those furnished by potash and soda.

The ordinary mode of exhibiting the production of the so-called *amalgam of ammonium* consists in acting upon the ammonium chloride (NH_4Cl) with sodium amalgam. A little pure mercury is heated in a test-tube, and a pellet of sodium thrown into it, when combination occurs with great energy. When the amalgam is nearly cool it may be poured into a larger tube containing a moderately strong solution of ammonium chloride; the amalgam at once swells to many times its bulk, forming a soft solid lighter than the water, which may be shaken out of the tube as a cylindrical mass, rapidly effervescing with evolution of NH_3+H, and soon recovering its original volume and liquid condition.

55. Ammonia is easily expelled from its salts by an alkali, so that an ammonium salt is easily detected by boiling the suspected substance with caustic soda, when the odour of ammonia will be perceived:

$$NH_4Cl + NaOH = NaCl + NH_3 + H_2O.$$

When an ammonium salt is heated it is split up into ammonia and the acid from which it is formed, ammonium chloride, for example, becoming ammonia and hydrogen chloride, $NH_4Cl=NH_3+HCl$†; but if these products be allowed to cool together, they combine again to produce the original salts. This behaviour furnishes an example of the

* This experiment is more conveniently made with a strong solution of ammonium sulphate in a common plate. A sheet of platinum connected with the positive pole of the battery (five or six Grove's cells) is immersed in the solution, and a piece of filter-paper is laid upon it, on which is a globule of mercury; the negative pole is plunged into the latter.

† Ammonium chloride does not dissociate if perfectly dry.

phenomenon called *dissociation*, which differs from decomposition in that the constituents into which a compound is *dissociated* by heat recombine if they are allowed to cool together; the products of the *decomposition* of a compound, on the other hand, do not so recombine.

The dissociation of ammonium chloride may be demonstrated by taking advantage of the low specific gravity of NH_3 as compared with that of HCl (NH_3 is $17 \cdot 2 = 8.5$, and HCl $36.5/2 = 18.25$ times heavier than H). On this account NH_3 diffuses more rapidly than HCl. A fragment of ammonium chloride is placed in a narrow test-tube with a plug of asbestos at a little distance above it, a piece of red litmus-paper is placed in the tube, and the ammonium chloride and the asbestos are heated; the NH_3, being lighter, diffuses through the asbestos before the HCl does, and blues the red litmus-paper, but soon after the HCl diffuses through, and the litmus is again reddened.

The *volatility* of ammonia and of the ammonium salts renders a solution of the gas useful as an alkali in cases, such as in analysis, where the *fixed* alkalies, potash, and soda, would be objectionable on account of their fixity. Ammonia finds application in making sodium carbonate (*q.v.*) and, as already explained, in freezing-machines.

Ammonia has a tendency to combine as a whole with many metallic salts, much as water does; a typical compound of this sort is $CuSO_4.5NH_3$. It readily loses ammonia when heated.

Although free nitrogen and hydrogen can only with difficulty be made to form ammonia by direct combination, this compound is produced when the nitrogen meets with hydrogen in the *nascent* state; that is, at the instant of its liberation from a combined form. Thus, if a few iron-filings be shaken with a little water in a bottle of air, so that they may cling round the sides of the bottle, and a piece of red litmus-paper be suspended between the stopper and the neck, it will be found to have assumed a blue colour in the course of a few hours, and ammonia may be distinctly detected in the rust which is produced. It appears that the water is decomposed by the iron in the presence of the carbonic acid of the air and water, and that the hydrogen liberated enters at once into combination with the nitrogen, held in solution by the water, to form ammonia.

56. For many years ammonia was the only compound of nitrogen with hydrogen which was known. Lately, two others have been discovered—namely, *hydrazine*, N_2H_4, a colourless gas, and *hydrogen nitride* (*hydrazoic acid*), N_3H, a volatile liquid, possessed, as its alternative name implies, of the properties proper to an acid. The importance of these compounds resides in the light which they throw upon the theory of organic nitrogen compounds, and can only be appreciated when these are being discussed. They have as yet received no practical application, and since they are prepared by the action of reducing agents on nitric acid or its derivatives, a further consideration of them will be found after the treatment of this subject.

57. *Production of nitrous and nitric acids from ammonia.*—If a few drops of a strong solution of ammonia are poured into a pint bottle, and ozonised air (from the tube for ozonising by induction, Fig. 47) is passed into the bottle, thick white clouds speedily form, consisting of *ammonium nitrite* (NH_4NO_2), the nitrous acid having been produced by the oxidation of the ammonia at the expense of the ozonised oxygen—

$$2NH_3 + O_3 = H_2O + NH_4NO_2.$$

If copper filings be shaken with solution of ammonia in a bottle of air, white fumes will also be produced, together with a deep blue solution containing copper oxide and ammonium nitrite; the act of oxida-

tion of the copper appearing to have induced a simultaneous oxidation of the ammonia.

A coil of thin platinum wire made round a pencil, if heated to redness at the lower end and suspended in a flask (Fig. 70) with a little strong ammonia at the bottom, will continue to glow for a great length of time, in consequence of the combination of the ammonia with the oxygen of the air at its surface, attended with great evolution of heat. Thick white clouds of NH_4NO_3 are formed, and frequently red vapour of nitrous anhydride (N_2O_3) itself. A coil of thin copper wire acts in a similar manner.

Fig. 70.

When a tube delivering oxygen is passed down to the bottom of the flask, the action is far more energetic, the heat of the platinum rising to whiteness, whereupon an explosion of the mixture of ammonia and oxygen ensues. After the explosion the action recommences, so that the explosion repeats itself as often as may be wished. It is unattended with danger if the mouth of the flask be pretty large, but it is advisable to surround the flask with a cylinder of coarse wire gauze. By regulating the stream of oxygen, the bubbles of that gas may be made to burn as they pass through the ammonia at the bottom of the flask.

The oxidation of ammonia may also be shown by the arrangement represented in Fig. 71. Air is slowly passed from the glass gas-holder B, through very weak ammonia in the bottle *a*, into a hard glass tube having a piece of red litmus-paper at *b* and a plug of platinised asbestos in the centre, heated by a gas-burner; a piece of blue litmus-paper is placed at *c*, and the tube is connected with a large globe (*d*). The red litmus at *b* is changed to blue by the ammonia, whilst the blue litmus at *c* is reddened by the nitrous acid produced

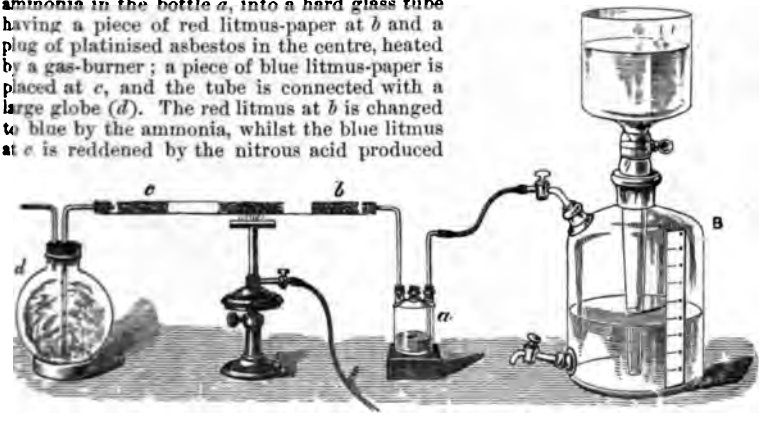


Fig. 71.—Oxidation of ammonia.

in its oxidation, and clouds of ammonium nitrite, accompanied by red nitrous fumes, appear in *d*. To obtain all the results in perfection, small quantities of ammonia must be successively introduced into *a*.

When hydrogen or coal gas burns in air, small quantities of nitrous and nitric acids are produced, apparently by the oxidation of atmospheric nitrogen.

58. In the presence of strong bases, and of porous materials to favour the change, ammonia may suffer further oxidation to nitric acid, which acts on the base to form a nitrate; thus, $2NH_3 + CaO + O_5 = Ca(NO_3)_2$ (calcium nitrate) $+ 3H_2O$.

It has already been seen that the rapid oxidation (combustion) of ammonia produces nitrogen and water.

This formation of nitrates from ammonia is commonly referred to as *nitrification*, and appears to be concerned in the formation of the

natural supplies of saltpetre which are of so great importance to the arts.*

It is brought about by a micro-organism (the nitrifying organism) which accelerates the oxidation of the ammonia produced by the decay of nitrogenous organic matter in the soil.

It would appear that at least two micro-organisms are concerned in the production of nitrates. The one induces the formation of nitrites from the ammonia, whilst the other induces oxididation of these to nitrates. Nitrification can only occur when some basic substance, like calcium carbonate, is present to neutralise the acids produced ; being dependent on a micro-organism, it can only proceed at temperatures which are not inhibitory to the life of the organism (between 0° and 55° C.). Darkness favours the process.

Compounds of Nitrogen and Oxygen.

59. Though these elements under ordinary conditions exhibit no attraction for each other, six compounds, which contain them in different proportions, have been obtained by different processes, viz. N_2O, NO, N_2O_3, NO_2, N_2O_5.

When a succession of strong electric sparks from the induction-coil is passed through atmospheric air in a dry flask (especially if the air be mixed with oxygen), a red gas, nitric peroxide (NO_2), is formed; if water be present this is absorbed and converted into nitrous and nitric acids; $2NO_2 + H_2O = HNO_2 + HNO_3$.

If the experiment be made in a U-tube having one limb surmounted by a stoppered globe into which platinum wires are sealed (fig. 72) filled with water coloured with blue litmus, the latter will very soon be reddened by the acid formed, and the air will be found to diminish very considerably in volume, eventually losing its power of supporting combustion, in consequence of the removal of oxygen.

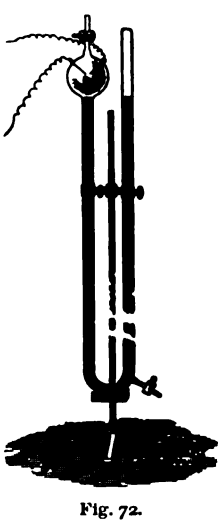


Fig. 72.

When a few inches of magnesium tape are burnt in a gas-jar of air, red fumes may be perceived on looking down the jar at the close of the combustion, and the presence of N_2O_3 or NO_2 may be shown by drawing the residual air through a mixture of potassium iodide with a little starch and acetic acid, when the iodine is set free and blues the starch. This renders it probable that the electric spark causes the combination of nitrogen and oxygen on account of its high temperature.

When ozonised air (p. 65) is passed into water, nitric acid is found in solution. Rain water contains about one part per million of nitric acid, in the form of nitrates.

When hydrogen gas, mixed with a small quantity of nitrogen, is burnt, the water collected from it is found to have an acid taste and reaction, due to the presence of a little nitric acid, resulting from the combination of the nitrogen with the oxygen of the air under the influence of the intense heat of the hydrogen flame.

Since all the compounds of nitrogen and oxygen are obtained, in practice, from nitric acid, the chemical history of that substance may conveniently that of the oxides of nitrogen.

* The charcoal which has been used in the sewer ventilators has been found to contain abundance of nitrates.

Nitric Acid, or Hydrogen Nitrate.

HNO_3 = 63 parts by weight = 2 volumes.

60. This most important acid is obtained from saltpetre, which is found as an incrustation upon the surface of the soil in hot and dry climates, as in some parts of India and Peru. The salt imported into this country from Bengal and Oude consists of potassium nitrate (KNO_3), whilst the Peruvian or Chilian saltpetre is sodium nitrate, or "nitrate" ($NaNO_3$). Either of these will serve for the preparation of nitric acid.

On the small scale, in the laboratory, nitric acid is prepared by distilling potassium nitrate with an equal weight of concentrated sulphuric acid.

As an experiment, 4 ounces of powdered nitre, thoroughly dried, are introduced into a stoppered retort (Fig. 73) and 2½ measured ounces of concentrated sulphuric acid poured upon it. As soon as the acid has soaked into the nitre, a gradually increasing heat is applied by an Argand burner, when the acid distils. It must be preserved in a stoppered bottle.

When the acid has ceased distilling, the retort should be allowed to cool, and filled with water. On heating for some time the saline residue will dissolve. The solution may then be poured into an evaporating dish, and evaporated to a small bulk. On allowing the concentrated solution to cool, crystals of bisulphate of potash or potassium hydrogen sulphate ($KHSO_4$) are deposited, a salt which is very useful in many metallurgical and analytical operations.

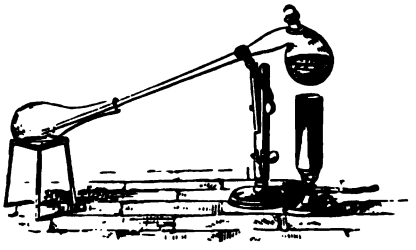


Fig. 73.—Preparation of nitric acid.

The decomposition of potassium nitrate by an equal weight of sulphuric acid is explained by the equation—

$$KNO_3 + H_2SO_4 = HNO_3 + KHSO_4.$$

It would appear at first sight that one-half of the sulphuric acid might be dispensed with, inasmuch as one molecule could be made to decompose two molecules of potassium nitrate, $2KNO_3 + H_2SO_4 = 2HNO_3 + K_2SO_4$, but it is found that when a smaller quantity of sulphuric acid is used, so high a temperature is required to effect the complete decomposition of the saltpetre (the above equation then representing only the first stage of the action), that much of the nitric acid is decomposed; and the normal potassium sulphate (K_2SO_4), which would be the final result, is not nearly so easily dissolved out of the retort by water as is the bisulphate.

For the preparation of large quantities of nitric acid, sodium nitrate is substituted for potassium nitrate, being much cheaper, and furnishing a larger proportion of nitric acid.

For the decomposition of the sodium nitrate can be represented by the above equation, if Na be substituted for K, and on comparing the equations it will be seen that 85 parts by weight of $NaNO_3$ yield the same quantity of HNO_3 as that yielded by 101 parts by weight of KNO_3.

The sodium nitrate is introduced into an iron cylinder (A, Fig. 74) and about five-sixths of its weight of sulphuric acid is poured upon it through a stoppered

opening at the back.* Heat is then applied by a furnace, into which the cylinders are built in pairs, when the nitric acid passes off in vapour, and is condensed in a series of stoneware bottles (B). surrounded with cold water. The commercial acid is liable to contain chlorine, hydrochloric acid, and iodic acid (from sodium chloride and iodate in the nitrate), sulphuric acid, sodium sulphate, nitrogen oxides, and iron. It is purified by redistillation. the middle portion of the distillate being pure.

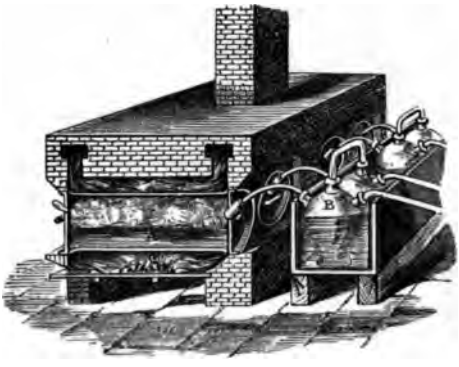


Fig. 74.—Preparation of nitric acid.

In the preparation of nitric acid, it will be observed at the beginning and towards the end of the operation that the retort becomes filled with a red vapour. This is due to the decomposition by heat of a portion of the colourless vapour of nitric acid, into water, oxygen, and nitric peroxide, $2HNO_3 = H_2O + O + 2NO_2$, this last forming the red vapour, a portion of which is absorbed by the nitric acid, and gives it a yellow colour (*red fuming nitric acid*). The pure nitric acid is colourless, but if exposed to sunlight it becomes yellow, a portion suffering this decomposition. In consequence of the accumulation of the oxygen in the upper part of the bottle, the stopper is often forced out suddenly when the bottle is opened, and care must be taken that drops of this very corrosive acid be not spirted into the face.

The strongest nitric acid (obtained by distilling perfectly dry nitre with an equal weight of pure oil of vitriol, and collecting the middle portion of the acid separately from the first and last portions, which are somewhat weaker) emits very thick grey fumes when exposed to damp air, because its vapour, though itself transparent, absorbs water very readily from the air, and condenses into very minute drops of dilute nitric acid which compose the fumes. The weaker acids commonly sold in the shops do not fume so strongly. A criterion of the strength of any sample of the acid is afforded by the specific gravity, which may be ascertained by the methods described for ammonia, using a hydrometer adapted for liquids heavier than water. Thus the strongest acid (HNO_3) has the specific gravity 1.52;† whilst the ordinary *aquafortis* or dilute nitric acid has the sp. gr. 1.29, and contains only 46 per cent. of HNO_3. The concentrated nitric acid usually sold by the operative chemist (*double aquafortis*) has the sp. gr. 1.41, and contains 67.5 per cent. of HNO_3.

A very characteristic property of nitric acid is that of staining the skin yellow. It produces the same effect upon most animal and vegetable matters, especially if they contain nitrogen. The application of

* To avoid difficulties due to frothing when strong H_2SO_4 is used, it is now customary to use a somewhat weaker acid (chamber acid, *q.v.*) and to redistil the less concentrated nitric acid obtained, with strong sulphuric acid.

† It is extremely difficult to obtain the HNO_3 free from any extraneous water, as it undergoes decomposition not only when vaporised at the boiling-point, but even at ordinary temperatures. Distillation in a vacuum is more successful.

this in dyeing silk a fast yellow colour may be seen by dipping a skein of white silk in warm dilute nitric acid, and afterwards immersing it in dilute ammonia, which converts the yellow colour into brilliant orange. When sulphuric or hydrochloric acid is spilt upon the clothes, a red stain is produced, and a little ammonia restores the original colour; but nitric acid stains are yellow, and ammonia intensifies instead of removing them, though it prevents the cloth from being eaten into holes.

Nitric acid changes most organic colouring matters to yellow, but, unless very concentrated, it merely reddens litmus. If solutions of indigo and litmus are warmed in separate flasks, and a little nitric acid added to each, the indigo will become yellow and the litmus red. Here the indigo (C_8H_5NO) acquires oxygen from the nitric acid, and is converted into *isatine* ($C_8H_5NO_2$).

When nitric acid is heated, it begins to boil at 86° C., but it cannot be distilled unchanged, for a considerable quantity is decomposed into nitric peroxide, oxygen, and water, the two first passing off in the gaseous form, whilst the water remains in the retort with the nitric acid, which thus becomes gradually more and more dilute, until it contains 68 per cent. of HNO_3, when it passes over unchanged, at the temperature of 248° F. (120° C.). The specific gravity of this acid is 1.42; its composition corresponds approximately with the hydrate $2HNO_3.3H_2O$. If an acid weaker than this be submitted to distillation, water will pass off until acid of this strength is obtained, when it distils unchanged. A similar result is obtained when dry air is passed through strong or weak nitric acid at 15° C.; an acid of 64 per cent. strength (corresponding with $HNO_3.2H_2O$) is produced in either case.

The specific gravity of the vapour of nitric acid, at 86° C., has been determined as 29.6 (H = 1), which is sufficiently near to half of 63 to warrant the formula HNO_3, for the molecule of nitric acid (p. 47).

The facility with which nitric acid parts with a portion of its oxygen renders it very valuable as an *oxidising agent*. Comparatively few substances which are capable of forming compounds with oxygen can escape oxidation when treated with nitric acid.

A small piece of phosphorus dropped into a porcelain dish containing the strongest nitric acid (and placed at some distance to avoid danger), is soon attacked by the acid, generally with such violence as to burst into flame, and sometimes to shatter the dish; the product is phosphoric acid, the highest state of oxidation of phosphorus.

When sulphur is heated with nitric acid, it is actually oxidised to a greater extent than when burnt in pure oxygen, for in this case it is converted into sulphurous anhydride (SO_2), whilst nitric acid converts it into sulphuric acid, H_2SO_4.

Charcoal, which is so unalterable by most chemical agents at the ordinary temperature, is oxidised by nitric acid. If the strongest nitric acid be poured upon finely powdered charcoal, the latter takes fire at once. Even iodine, which is not oxidised by free oxygen, is converted into iodic acid (HIO_3) by nitric acid.

But it is especially in the case of metals that the oxidising powers of nitric acid are called into useful application.

If a little black oxide of copper be heated in a test-tube with nitric

acid, it dissolves, without evolution of gas, yielding a blue solution, which contains copper nitrate, $2HNO_3 + CuO = H_2O + Cu(NO_3)_2$.

But when nitric acid is poured upon metallic copper (copper turnings), very violent action ensues, red fumes are abundantly evolved, and the metal dissolves in the form of copper nitrate, nitric oxide being formed, $8HNO_3 + Cu_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO$. The nitric oxide itself is colourless, but as soon as it comes into contact with the oxygen of the air, it is converted into the red nitric peroxide, $NO + O = NO_2$.

A certain amount of nitric peroxide is always produced directly by the action of copper on nitric acid, the proportion depending upon the concentration of the acid and the ratio of acid to copper. When excess of concentrated nitric acid is used the gas consists of NO_2 (with about 10 per cent. of N_2O_3) and contains no NO; on the other hand, when the acid is diluted with twice its volume of water nearly pure NO is evolved. The following view, although it may not represent the actual course of the chemical change, is useful in expounding the nature of the action. Since nitric acid tends to decompose into $H_2O, 2NO_2$ and O, two molecules of the acid might be expected to oxidise one atom of copper, $Cu + 2HNO_3 = CuO + H_2O + 2NO_2$; the copper oxide would immediately react with another portion of the nitric acid to give copper nitrate, $CuO + 2HNO_3 = Cu(NO_3)_2 + H_2O$. When more copper is present the NO_2 might be expected to be reduced to NO, $Cu + NO_2 = CuO + NO$, the copper oxide dissolving as before. Since NO_2 reacts with water to form nitrous (and nitric) acid, little would be expected in the gas from a dilute nitric acid, but the proportion of NO would be expected to be increased because the reduction of the NO_2 would be more possible when it could not escape from the solution as gas.

It has been shown that nitric acid which is free from nitrous acid (always present in commercial samples) has a very tardy, if any, action on many metals, so that it would seem as if the oxidation were really effected by the nitrous acid. A very small quantity of this suffices to start the action, because the nitric oxide produced reduces another portion of the nitric acid to nitrous acid, thus serving as a carrier of oxygen from the nitric acid to the metal.

By the action of metals on nitric acid of various strengths all the reduction products of nitric acid—namely, the oxides of nitrogen, nitrogen, hydroxylamine, hyponitious acid, and ammonia—can be obtained. Those metals whose attraction for oxygen is feeble (those which do not decompose water, or only do so at a very high temperature, p. 21) do not reduce HNO_3 to a lower state of oxidation than NO; those metals which decompose water at a red heat yield all the reduction products; whilst those which decompose water either at the ordinary temperature or below a red heat yield even hydrogen. The nature of the products varies with the state of dilution, and with the temperature. Silver behaves like copper with nitric acid. Iron evolves nearly pure NO when dissolved in nitric acid diluted with either one part or 12 parts of water. Zinc, with 1 : 2 strength of acid (hot or cold) evolves nearly equal volumes of NO and N_2O, but with the strong acid it evolves scarcely any NO, but a mixture of about 2 volumes N_2O and 1 volume N; with dilute nitric acid zinc yields ammonia (which of course remains combined with the nitric acid in the form of ammonium nitrate), possibly produced by the action of hydrogen, liberated by the dissolution of the metal in the acid (just as when zinc is dissolved in dilute sulphuric acid), on the nitric acid, $HNO_3 + H_8 = 3H_2O + NH_3$.

Though all the metals in common use, except gold and platinum, are *oxidised* by nitric acid, they are not all *dissolved;* aluminium is superficially oxidised but not further attacked; tin and antimony are left by the acid in the state of insoluble oxides, which possess acid properties and do not unite with nitric acid. When concentrated nitric acid is poured upon tin, no action is observed;* but on adding a little water, NO_2 is evolved in abundance, and the tin is converted into a white powder, metastannic acid. On stirring this white mixture with slaked lime the smell of ammonia is perceived, this gas having been liberated from ammonium

* This is often noticed in the case of strong nitric acid, and is possibly to be explained by supposing that the nitrous acid present is rapidly used up and cannot be re-formed in such a concentrated acid (see above). The strongest nitric acid which has been obtained is without action on chalk, even when boiled therewith.

nitrate by the lime. Thus tin reduces even moderately strong nitric acid to ammonia.

When a solution of potassium nitrate is mixed with a strong solution of caustic potash, and heated with granulated zinc, ammonia is abundantly disengaged, being produced by the nascent hydrogen from the action of the zinc upon the caustic potash. Aluminium acts thus even in dilute solutions.

Nitric acid is completely reduced, yielding only nitric oxide, when shaken with strong sulphuric acid and mercury. On this fact is based the application of the *nitrometer* (Fig. 75) for estimating the quantity of a nitrate present in a substance. The apparatus is filled with mercury by opening the stop-cock and pouring the metal into the open limb. The stop-cock having been closed, the right-hand limb is lowered so that the mercury in it may be at a lower level than that in the other limb. The solution to be tested is poured into the cup and sucked into the graduated limb by opening the stop-cock until all liquid has passed through, care being taken not to admit air. Oil of vitriol is next sucked in, in a similar manner, and the closed limb is thoroughly shaken to mix the mercury with the solution and acid. Nitric oxide is rapidly evolved, and when no more is seen to collect in the graduated tube, the mercury is brought to the same level in each limb, as shown in the cut, and the volume of nitric oxide is read by means of the graduations on the tube. The stop-cock has two holes bored in it, so that the apparatus may be washed out through the small tube beside the cup. The weight of nitric acid present may be calculated from the volume of nitric oxide measured, for 63 grams of nitric acid (HNO_3) yield 22.22 litres of nitric oxide (NO) at 760 mm. pressure and 0° C.

Fig. 75.—Nitrometer.

All the metals in common use are attacked by nitric acid, except gold, platinum, and, in less degree, aluminium, so that this acid is used to distinguish and separate these metals from others of less value. The ordinary ready method of ascertaining whether a trinket is made of gold consists in touching it with a glass stopper wetted with nitric acid, which leaves gold untouched, but colours base alloys blue, from the formation of copper nitrate. The *touch-stone* allows this mode of testing to be applied with great accuracy. It consists of a species of black basalt, obtained chiefly from Silesia. If a piece of gold be drawn across its surface, a golden streak is left, which is not affected by moistening with nitric acid; whilst the streak left by brass, or any similar base alloy is rapidly dissolved by the acid. Experience enables an operator to determine, by means of the touch-stone, pretty nearly the amount of gold present in the alloy, comparison being made with the streaks left by alloys of known composition.

Action of nitric acid on organic substances.—The oxidising action of nitric acid on some organic substances is so powerful as to be attended with inflammation; if a little of the strongest acid be placed in a porcelain capsule, and a few drops of oil of turpentine be poured into it

from a test-tube fixed to the end of a long stick, the turpentine takes fire with a sort of explosion. By boiling some of the strongest acid in a test-tube (Fig. 76), the mouth of which is loosely stopped with a plug of raw silk or of horse-hair, the latter may be made to take fire and burn brilliantly in the vapour of nitric acid.

In many cases the products of the action of nitric acid exhibit a most interesting relation to the substances from which they have been produced, one or more atoms of the hydrogen of the original compound having been removed in the form of water by the oxygen of the nitric acid, whilst the spaces thus left vacant have been filled up by the nitric peroxide resulting from the de-oxidation of the nitric acid, producing what is termed a *nitro-substitution* compound. A very simple example of this displacement of H by NO_2, is afforded by the action of nitric acid upon benzene. A little concentrated nitric acid is placed in a flask, and benzene cautiously dropped into it; a violent action ensues, and the acid becomes of a deep red colour; if the contents of the flask be now poured into a large vessel of water, a heavy yellow oily liquid is separated, having a powerful odour, like that of bitter almond oil. This substance, which is used to a considerable extent in perfumery under the name of essence of Mirbane, is called *nitro-benzene*, and its formula, $C_6H_5(NO_2)$, at once exhibits its relation to benzene, C_6H_6.

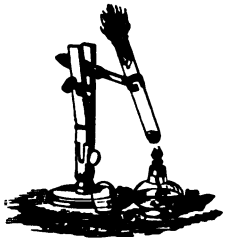


Fig. 76.

To understand the nature of this reaction the *theory of radicles and of substitution* must be realised. Just as the molecules of most elements may be regarded as consisting of two parts, neither of which is capable of a separate existence, so the molecules of most compounds may be looked upon as composed of two or more parts or *radicles*, none of which can exist alone. Water, for example, consists of the radicles H– and –OH, united by one "bond" from each, which bond causes the radicle to enter into a new combination immediately it is liberated. The acids which contain oxygen, or *oxy-acids*, consist of one or more *hydroxyl* (– OH) *radicles* and an *acid radicle*. Thus nitric acid is $NO_2{\cdot}OH$, containing the acid-radicle *nitroxyl* (NO_2) and one hydroxyl radicle.

Such radicles take part in chemical reactions, and may be substituted for elements, as though they were themselves elements. Thus when the hydroxyl radicle exists in one of the reacting substances it may be expected to occur in one of the products, unless the reaction be of so drastic a character as to break up the radicles of the reacting substances. It follows that a large number of chemical changes (particularly in organic chemistry) are to be explained as exchanges between the radicles of compounds, in the same way that many are to be explained as exchanges between the elementary atoms constituting the reacting compounds—*e.g.*, $KI + HCl = KCl + HI$.

Benzene contains the radicle C_6H_5, so that the reaction between benzene and nitric acid may be represented as an exchange of the C_6H_5 radicle of the benzene for the OH radicle of the nitric acid, the nitroxyl radicle having been substituted for hydrogen in the benzene, $H{\cdot}C_6H_5 + NO_2{\cdot}OH = NO_2{\cdot}C_6H_5 + H{\cdot}OH$.

It is by an action of this description that nitric acid gives rise to gun-cotton, and other explosive substances of the same class, when acting upon the different varieties of woody fibre, as cotton, paper, saw-dust, &c. For making these, nitric acid finds extended application.*

61. *Nitrates.*—Its powerful action on bases places nitric acid among the strongest of the acids, though the disposition of its elements to assume the gaseous state at high temperatures, conjoined with the feeble attraction existing between nitrogen and oxygen, causes its salts to be decomposed, without exception, by heat.

The nature of the decomposition varies with the metal contained in the nitrate. The nitrates of alkali metals are first converted into nitrites by the action of heat: thus KNO_3 gives KNO_2 and O; the nitrites themselves being eventually decomposed, evolving nitrogen and oxygen, and leaving the oxide of the metal. The nitrates of copper and lead evolve nitric peroxide (NO_2) and oxygen, the oxides being left. The nitrate of mercury leaves red oxide of mercury, which is decomposed at a higher temperature into mercury and oxygen.

Nitric acid is a *monobasic* acid, because it contains only one atom of hydrogen which can be exchanged for a metal. It will be found that it is only the H of the OH radicles in an oxy-acid which can be exchanged for metals; the OH groups may thus be said to impart an acid character to a compound. Comparatively few of the nitrates are in common use; they will be mentioned under the metals of which they are the salts.

The oxidising effects of nitric acid are shared to some extent by the nitrates. A mixture of nitrate of lead with charcoal explodes when sharply struck, from the sudden evolution of carbonic acid gas, produced by the oxidation of the carbon. If a few crystals of copper nitrate be sprinkled with water and quickly wrapped up in tinfoil, the latter will, after a time, be so violently oxidised as to emit brilliant sparks.

But in the case of the nitrates of alkali metals, the oxidation takes place only at a high temperature. If a little nitre be fused in an earthen crucible or an iron ladle, and, when it is at a red heat, some powdered charcoal, and afterwards some flowers of sulphur, be thrown into it, the energy of the combustion will testify to the violence of the oxidation. In this manner the carbon is converted into potassium carbonate (K_2CO_3), and the sulphur into potassium sulphate (K_2SO_4). (See *Gunpowder.*)

Determination of the composition of nitric acid.—A definite weight, say 10 grams, of pure lead oxide is mixed with 5 grams of nitric acid, and the mixture is gently heated as long as vapour of water escapes; $PbO + 2HNO_3 = H_2O + Pb(NO_3)_2$. Say that the residue weighs 14.27 grams; then

From the weight of lead oxide and nitric acid . .	15.00 grams
Deduct weight of lead oxide and lead nitrate . .	14.27 „
Water which has been expelled	0.73

corresponding with $\frac{0.73}{9}$ or 0.08 gram H.

The mixture of lead nitrate and excess of lead oxide is then strongly heated in a tube containing copper, when $Pb(NO_3)_2 + Cu_5 = PbO + 5CuO + N_2$; the nitrogen is collected and measured. Say that 884.7 c.c. of N are obtained; these weigh $884.7 \times \frac{14}{11110}$ gram = 1.19 gram, since 11110 c.c. of N weigh 14 grams.

Hence we find, in 5 grams of nitric acid, 1.11 gram N, 0.08 gram H, and, by difference, 3.73 grams O. Dividing these numbers by the atomic weights, 14, 1, and 16, we obtain 0.08 atom of N, 0.08 atom of H, and 0.24 atom of O, or 1 atom of H to 1 atom of N and 3 atoms of O. This would give, for the molecule of nitric acid, HNO_3, 1 + 14 + 48 = =63, a result agreeing from that obtained from the sp. gr. of its vapour (see page 91).

* It is stated that nitrous acid in the nitric acid exerts the same kind of influence in substitution reactions of nitric acid as it exerts in the action of the acid on metals (p. 92).

62. **Anhydrous nitric acid** or **nitric anhydride** (N_2O_5) is obtained by gently heating silver nitrate in a slow current of chlorine, great care being taken to exclude every trace of water; $2AgNO_3 + Cl_2 = 2AgCl + O + N_2O_5$.

It may also be obtained by adding anhydrous phosphoric acid to the strongest nitric acid cooled in snow and salt, and carefully distilling at as low a temperature as possible. The distillate separates into two layers, the lower of which is a compound $2N_2O_5.H_2O$, called *dinitric acid;* the upper layer is separated and cooled.

The anhydride is condensed as a crystalline solid. It forms transparent colourless prisms which melt at 30° C., and boil at 47° C. By a slightly higher temperature it is readily decomposed; and it has been said to decompose even at the ordinary temperature, in sealed tubes which were shattered by the evolved gas. It is more stable in the dark. When the anhydride is brought in contact with water, much heat is evolved, and nitric acid, $H_2O.N_2O_5$, is produced.

The specific gravity of the vapour of nitric anhydride being unknown, it is only a surmise that its molecule is represented by N_2O_5.

63. **Nitrous oxide** or **laughing gas** ($N_2O = 44$ parts by weight $= 2$ volumes) is prepared by heating ammonium nitrate, when it is resolved with evolution of heat, into water and nitrous oxide; $NH_4NO_3 = 2H_2O + N_2O$.

To obtain nitrous oxide, an ounce of ammonium nitrate may be *gently* heated in a small retort, when it melts, boils, and gradually disappears entirely in the forms of steam and nitrous oxide. The latter may be collected with slight loss over water.

In the preparation of nitrous oxide, if the temperature be too high, the gas may contain nitric oxide and nitrogen; $NH_4NO_3 = NO + N + 2H_2O$. Moreover, since 80 grams (1 gram-molecule) of NH_4NO_3 evolve some 31,000 gram-units of heat when decomposed into H_2O and N_2O, explosion is liable to occur. To purify the gas, it should be passed through a strong solution of ferrous sulphate, to absorb the nitric oxide, and afterwards through potash to absorb acid vapours.

Nitrous oxide is colourless, but has a slight odour and a sweetish taste. Its characteristic anæsthetic property is well known. It accelerates the combustion of a taper like oxygen itself, and will even kindle into flame a spark at the end of a match, for it is readily decomposed into N_2 and O by the temperature of burning wood. When C is burnt into CO_2 by $2N_2O$, it evolves 36,000 more units of heat than when burnt in O_2, showing that, contrary to the usual law, heat is *evolved* in the *decomposition* of the N_2O, amounting to 18,000 units per molecule. Such a compound is said to be *endothermic*, whilst a compound like water, which is formed with evolution of heat is called *exothermic*. Nitrous oxide can readily be distinguished from oxygen by shaking it with water, which absorbs, at the ordinary temperature, about three-fourths of its volume of the nitrous oxide. It is absorbed in larger quantity by alcohol. It is also much heavier than oxygen, its specific gravity being 1.53, and is liquefied by a pressure of 40 atmospheres at 7° C, and solidified at −115° C. The liquid is now sold in wrought-iron vessels for use as an anæsthetic in dental surgery. In small doses it has an intoxicating effect, whence its title of "laughing gas."

The liquid nitrous oxide has a very low refractive index; its sp. gr. is 0.94 at 0° C., and it boils at −90° C. A lighted match thrown into the liquid burns with great brilliancy. When it is mixed with carbon bisulphide and evaporated *in vacuo*, the temperature falls to −140° C. The critical temperature of N_2O is 39° C., and the critical pressure is 73 atmos.

64. **Nitric oxide** ($NO = 30$ parts by weight $= 2$ volumes) is usually obtained by the action of copper upon diluted nitric acid (see page 146).

Twenty grams of copper turnings or clippings are introduced into a retort,

and 85 c.c. of a mixture of concentrated nitric acid with an equal volume of water are poured upon them. A very gentle heat may be applied to assist the action, and the gas may be collected over water (see Fig. 109), which absorbs the red fumes (NO_2) formed by the union of the NO with the oxygen of the air contained in the retort.

The nitric oxide prepared by the action of copper on nitric acid generally contains nitrous oxide. Pure nitric oxide may be obtained by heating in a retort 6.5 grams potassium nitrate, 65 grams of ferrous sulphate, and 85 c.c. of dilute sulphuric acid (containing one measure of acid to three measures of water), which will yield about 1133 c.c. of gas; $2KNO_3 + 6FeSO_4 + 4H_2SO_4 = K_2SO_4 + 3Fe_2(SO_4)_3 + 2NO + 4H_2O$.

Nitric oxide is distinguished from all other gases by the production of a red gas, when the colourless nitric oxide is allowed to come in contact with uncombined oxygen, the presence of which, in mixtures of gases, may be readily detected by adding a little nitric oxide. The red gas consists chiefly of nitric peroxide (NO_2) when the oxygen is in excess, otherwise it contains also some nitrous anhydride (N_2O_3).

The combination of nitric oxide with oxygen may be exhibited by decanting a pint bottle of oxygen, under water, into a tall jar filled with water coloured with blue litmus, and adding to it a pint bottle of nitric oxide (Fig. 77). Strong red fumes are immediately produced, and on gently agitating the cylinder, the fumes are absorbed by the water, reddening the litmus. The oxygen will now have been reduced to half its volume, and if another pint of nitric oxide be added, the remainder of the oxygen will be absorbed, showing that *two volumes of nitric oxide combine with one volume of oxygen*, forming nitric peroxide which is absorbed by the water. In presence of water and excess of oxygen, NO is entirely converted into nitric acid; $2NO + H_2O + O_3 = 2HNO_3$.

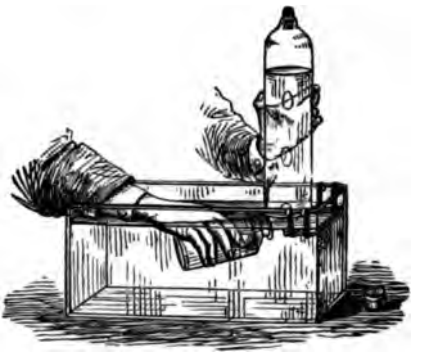


Fig. 77.

The addition of nitric oxide to atmospheric air was one of the earliest methods employed for removing the oxygen in order to determine the composition of air; but important variations were observed in the results, in consequence of the occasional formation of N_2O_3 in addition to the NO_2.

In all its properties nitric oxide is very different from nitrous oxide. It is much lighter, having almost exactly the same specific gravity as air, viz., 1.04, and is not dissolved to an important extent by water. It is more difficult to liquefy, for its critical temperature is $-93°$ C.; its boiling point is $-153°$ C. When a lighted taper is immersed in nitric oxide it is extinguished, although this gas contains twice as much oxygen as nitrous oxide, which so much accelerates the combustion of a taper, for the elements are held together by a stronger attraction in the nitric oxide, so that its oxygen is not so readily available for the support of combustion. (The nitric oxide prepared from copper and nitric acid sometimes contains so much nitrous oxide that a taper burns in it brilliantly.) Even phosphorus, when just kindled, is extinguished in nitric oxide, but when allowed to attain to full combustion in air, and, therefore, to a temperature high enough to decompose the nitric oxide into N and O, it burns with extreme brilliancy in the

gas. Indeed, nitric oxide appears to be the least easy of decomposition of the whole series of oxides of nitrogen, which accounts for its being the most common result of the decomposition of the other oxides. Nitrous oxide itself, when passed through a red-hot tube, is partly converted into nitric oxide; and when a taper burns in a bottle of nitrous oxide, the upper part of the bottle is often filled with a red gas, indicating the formation of nitric oxide, and its oxidation by the air entering the bottle.

The difference in the stability of the two gases is also shown by their behaviour with hydrogen. A mixture of nitrous oxide with an equal volume of hydrogen explodes when in contact with flame, yielding steam and nitrogen, but a mixture of equal volumes of nitric oxide and hydrogen burns quietly in air, the hydrogen not decomposing the nitric oxide except at the temperature of a strong electric spark. An excess of hydrogen, however, is capable of decomposing nitric oxide, ammonia and water being formed.

If two volumes of nitric oxide are mixed with five volumes of hydrogen and the gas passed through a tube having a bulb filled with platinised asbestos (Fig. 78),* the mixture issuing from the orifice of the tube produces the red gas by contact with the air, which will strongly redden blue litmus; but if the platinised asbestos is heated with a spirit-lamp, the hydrogen, encouraged by the action of the platinum (p. 87), decomposes the nitric oxide, and strongly alkaline vapours of ammonia are produced, restoring the blue colour to the reddened litmus; $NO + H_5 = NH_3 + H_2O$. It will be remembered that when oxygen is in excess, ammonia is converted, under the influence of platinum, into water and nitrous acid (p. 87).

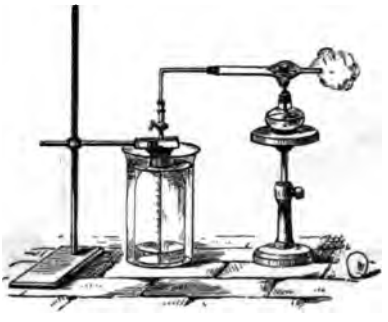


Fig. 78.

Nitric oxide is readily absorbed by ferrous salts, with which it forms dark brown solutions. If a little solution of ferrous sulphate ($FeSO_4$) be shaken in a cylinder of nitric oxide closed with a glass plate, the gas will be immediately absorbed and the solution will become dark brown. On applying heat, the brown compound is decomposed.

When shaken with moist ferrous hydroxide, NO is reduced to N_2O and N. In the presence of caustic soda, sodium hyponitrite ($Na_2N_2O_2$) and ammonia are also produced. By employing a large excess of soda, one-fifth of the nitric oxide may be converted into the hyponitrite.

65. **Nitrous anhydride** (N_2O_3 or $NO.NO_2 = 76$ parts by weight).—Ammonium nitrite is said to exist in minute quantity in rain water, and nitrites are occasionally found in well-waters, where they have probably been formed by the oxidation of ammonia (p. 87). Small quantities of ammonium nitrite appear to be formed by the combustion in air of gases containing hydrogen, this element uniting with the atmospheric oxygen and nitrogen.

Nitrous anhydride may be obtained by heating starch with nitric

* Asbestos which has been wetted with solution of platinic chloride, dried, and heated to redness, to reduce the platinum to the metallic state.

acid, but the most convenient process consists in gently heating nitric acid (sp. gr. 1.35) with an equal weight of white arsenic, and passing the gas, first through a U-tube (Fig. 79) surrounded with cold water, to condense undecomposed nitric acid, then through a similar tube containing calcium chloride to absorb aqueous vapour, and afterwards into a U-tube surrounded with ice. Through a small tube opening into the bend of this U-tube, the condensed nitrous anhydride drops into a tube drawn out to a narrow neck, so that it may be drawn off and sealed by the blow-pipe—

$$4HNO_3 + \underset{\text{White arsenic.}}{As_4O_6} + 4H_2O = 4\underset{\text{Arsenic acid.}}{H_3AsO_4} + 2N_2O_3.$$

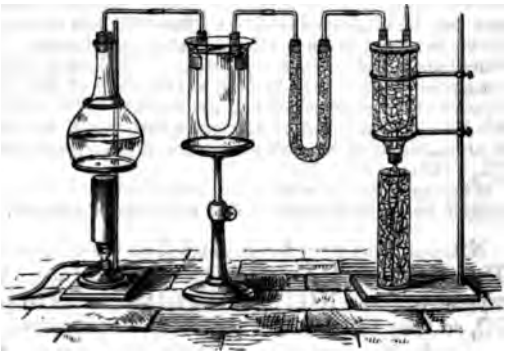


Fig. 79.—Preparation of nitrous anhydride.

The white arsenic is here used merely as a *reducing agent* to remove oxygen from the nitric acid. N_2O_3 is the anhydride of nitrous acid, HNO_2 ($H_2O.N_2O_3$); this acid is so unstable that it immediately breaks up into H_2O and N_2O_3: $2HNO_2 = H_2O + N_2O_3$. The object of the above reaction, therefore, is to remove two atoms of oxygen from two molecules of nitric acid—$2HNO_3 = H_2O + N_2O_3 + O_2$. White arsenic, As_4O_6, is arsen*ious* anhydride and readily oxidises to arsen*ic* anhydride, As_4O_{10}, which then combines with water to form arsenic acid $6H_2O.As_4O_{10} (= 4H_3AsO_4)$. Hence one molecule of white arsenic combines with four atoms of oxygen and will therefore reduce four molecules of nitric acid. The student should endeavour to sift in this manner all chemical equations which appear to him complex.

Nitrous anhydride is also prepared by decomposing the acid nitrosyl sulphate (see *Aqua regia*) with a small quantity of water—

$$2NOHSO_4 + H_2O = 2H_2SO_4 + N_2O_3.$$

If the gas liberated in these reactions be cooled to -20° C., a pure indigo-blue liquid, supposed to be N_2O_3, is formed; but if the temperature be allowed to rise the colour becomes dirty and the liquid is a mixture of nitrogen tetroxide (nitric peroxide), N_2O_4, and nitrous anhydride. It boils below the ordinary temperature giving a red gas which consists of equal volumes of nitric oxide and nitric peroxide, the proportion of the latter gradually increasing until the remaining liquid has the green colour and the composition of N_2O_4. It thus seems that N_2O_3 can only exist at low temperatures and in the liquid condition. The liquid is readily obtained, although not quite pure, by passing nitric oxide into cooled liquid nitrogen tetroxide. But when equal volumes of NO and NO_2 gases are mixed, no contraction occurs, as would be the case if they combined to N_2O_3; NO (2 volumes) + NO_2 (2 volumes) = N_2O_3 (2 volumes).

Water at about 0° C. dissolves nitrous anhydride, yielding a blue solution, which, as the temperature rises, becomes a solution of nitric acid, nitric oxide escaping with effervescence;

$$3N_2O_3 + H_2O = 2HNO_3 + 4\,NO.$$

The blue solution is believed to contain *nitrous acid*, HNO_2, or

NO.OH; $N_2O_3 + H_2O = 2HNO_2$; but this compound has not been obtained in a pure state. A very dilute solution of the acid may be preserved for some time, and even distilled, without decomposition.

The salts of nitrous acid, or *nitrites*, are interesting on account of their production from the nitrates by the action of heat (p. 95).

When potassium nitrate is fused in a fire-clay crucible and heated to redness, it evolves bubbles of oxygen, and slowly becomes potassium nitrite (KNO_2). The heat may be continued until a portion removed on the end of an iron rod, and dissolved in water, gives a strongly alkaline solution. The fused mass may then be poured upon a *dry* stone, and, when cool, broken into fragments and preserved in a stoppered bottle. On heating a fragment of the nitrite with dilute H_2SO_4, red vapours are disengaged, but these contain little nitrous acid, the greater part of this being decomposed by the water into HNO_3 and NO. When nitrous acid acts on ammonia, both compounds are decomposed, water and nitrogen being produced; $NH_2 + HNO_2 = N_2 + 2H_2O$.

When solutions of nitrites are heated in contact with air, they gradually absorb oxygen, becoming converted into solutions of nitrates.

Nitrous acid may be regarded as a solution of NO and NO_2 in water ($H_2O.N_2O_3$ or $H_2O.NO.NO_2$). The former tends to combine with oxygen to form NO_2, and the latter tends to part with oxygen to form NO, so that nitrous acid can behave, according to circumstances, either as a reducing agent or an oxidising agent. Obviously any compound capable of parting with oxygen to NO cannot obtain oxygen under the same circumstances from NO_2.

Nitrous acid reduces potassium permanganate, but oxidises ferrous sulphate. It will also oxidise the hydrogen of hydriodic acid (HI), thereby liberating the iodine; since a very small quantity of the latter can be detected by taking advantage of its property of bluing starch, the addition of hydriodic acid (KI and H_2SO_4) to nitrous acid ($KNO_2 + H_2SO_4$) forms a very delicate test for the latter: $HI + NO{\cdot}OH = H{\cdot}OH + I + NO$.

66. **Nitric peroxide** ($NO_2 = 46$ parts by weight, or $N_2O_4 = 92$ parts = 2 volumes).—By passing a mixture of nitric oxide with half its volume of oxygen, free from every trace of moisture, into a perfectly dry tube cooled in a mixture of ice and salt, the dark red gas is condensed into colourless prismatic crystals which melt at −12° C. into a nearly colourless liquid. This gradually becomes yellow as the temperature rises, and at 15° C. has a deep orange colour. It is very volatile, boiling at 71° F. (22° C.), to a red-brown vapour, which was long mistaken for a permanent gas, on account of the great difficulty of condensing it when once mixed with air or oxygen. Nitric peroxide is also obtained, mixed with one-fourth of its volume of oxygen, by heating lead nitrate (Fig. 80); $Pb(NO_3)_2 = PbO + 2NO_2 + O$.

Fig. 80.—Preparation of nitric peroxide.

The vapour of nitric peroxide is much heavier than atmospheric air.

Its vapour density diminishes as the temperature rises. At 140° C. the gas is 23 times as heavy as hydrogen, showing its molecular weight to be 46. This variation in density, in conjunction with the other changes with increase of temperature, leads to the belief that the molecule of nitric peroxide at low temperatures (in its liquid state) is N_2O_4, and becomes dissociated into $2NO_2$ at high temperatures. At 500° C. the gas becomes nearly colourless, being almost entirely dissociated into NO and O.

NO_2 is absorbed by many finely divided metals, forming compounds called *nitro-metals*. These are very unstable, and yield most of the reactions of NO_2.

Nitro-copper, Cu_2NO_2, is obtained when NO_2 is passed over freshly reduced Cu at 30° C.

By mixing N_2O_3 with the green liquid obtained by condensing the vapours from the action of HNO_3 on As_4O_6 the N_2O_3 contained in the liquid is converted into N_2O_4; $N_2O_3 + N_2O_3 = 2N_2O_4$.

Its colour varies with the temperature, becoming very dark at 100° F. (30° C.). The smell of the vapour is very characteristic. The vapour supports the combustion of strongly burning charcoal or phosphorus, and oxidises most of the metals, potassium taking fire in it spontaneously. Nitric peroxide must, therefore, rank as a powerful oxidising agent, and it is the presence of this substance in considerable proportion in the red fuming nitric acid that imparts to it higher oxidising powers than those of the colourless nitric acid. This red acid, the so-called *nitrous acid* of commerce, is prepared by introducing sulphur into the retorts containing the mixture of sodium nitrate and sulphuric acid employed in the preparation of the nitric acid, a portion of which is de-oxidised by the sulphur and converted into nitric peroxide.

Water in excess immediately decomposes nitric peroxide into nitrous acid and nitric acid, $2NO_2 + H_2O = HNO_3 + HNO_2$, so that the peroxide is not an independent anhydride.

When water is gradually added to liquid nitric peroxide, the liquid effervesces from escape of nitric oxide, and becomes green, blue, and ultimately colourless; $3NO_2 + H_2O = NO + 2HNO_3$. If the red nitric acid of commerce be gradually diluted with water, it will be found to undergo similar changes, always becoming colourless at last. The nitric acid which has been used in a Grove's battery has a green colour, from the large amount of nitric peroxide which has accumulated in it, in consequence of the decomposition of the acid by the hydrogen disengaged during the action of the battery; $H + HNO_3 = H_2O + NO_2$. If this green acid be diluted with a little water it becomes blue, and a larger quantity of water renders it colourless, causing the evolution of nitric oxide. Similar colours are obtained by passing nitric oxide into nitric acid of different degrees of concentration, apparently because nitric peroxide is formed and dissolved by the acid.

When silver, mercury, and some other metals are dissolved in cold nitric acid, a green or blue colour is often produced, leading a novice to suspect the presence of copper, the colour being really caused by the dissolution, in the unaltered nitric acid, of the nitric peroxide, produced by the de-oxidation of another portion.

The facility with which nitrous anhydride and nitric peroxide can be decomposed with formation of nitric oxide renders it probable that they really contain this group of elements as a radicle *nitroxyl*, NO. To express this they may plausibly be represented as formed on the same plan as that on which a molecule of water is formed. Just as in H – O – H, the two atoms of hydrogen are linked together by the diatomic oxygen, so in nitrous anhydride, O = N – O – N = O, two molecules of nitric oxide are linked together by the atom of oxygen, whilst in nitric peroxide (N_2O_4) a molecule of NO is bound up with a molecule of NO_2, thus, $O=N-O-N\begin{matrix}O\\O\end{matrix}$. If nitric anhydride be represented by $\begin{matrix}O\\O\end{matrix}\!\!>\!N-O-N\begin{matrix}O\\O\end{matrix}$, it is easy to understand the behaviour of these three oxides with the alkalies. Thus, by the action of nitrous anhydride on caustic potash, potassium nitrite K – O – N = O, in which K is substituted for O : N –, is formed, whilst nitric anhydride gives potassium nitrate $K-O-NO_2$, and nitric peroxide gives a mixture of

both salts. The remaining oxide of nitrogen N_2O may be represented as N.O.N
\\//

Such formulæ as the above are termed *structural formulæ*, since they essay to represent the way in which the molecule is built up, so far as it is possible to represent a three-dimensional structure on one plane. They must be written with due regard to the valency of the elements; thus nitrogen should always appear either as trivalent or pentavalent, for its atom-linking power has always one or other of these values. They must also be written with regard to the *constitution* of the compound, that is, the relationships which the various atoms show towards each other; thus, since there is evidence that the nitrogen atom and two of the oxygen atoms in nitric acid behave as the radicle NO_2, no structural formula failing to represent the N as directly attached to two oxygen atoms could be accepted.

All the oxides of nitrogen are endothermic compounds (p. 96), which accounts for the indisposition of N and O to combine directly. The following equations represent the number of calories or gram-units of heat (p. 44) evolved by the decomposition of one gram-molecule (the molecular weight expressed in grams) of N_2O, NO and NO_2:

$$N_2O = N_2 + O - 18{,}000 \text{ cal.}$$
$$NO = N + O - 21{,}500 \text{ ,,}$$
$$NO_2 = N + O_2 - 7650 \text{ ,,}$$

The general principle upon which the determination of the composition of these oxides has been determined is the decomposition of a measured volume of the gaseous oxide either by heat alone, or by burning some oxidisable substance in it, and measuring and analysing the volume of the gases or gas obtained.

Thus, when *nitrous oxide* is passed through a red-hot tube, its volume is increased by one-half, the gas becoming a mixture of 1 volume of oxygen and 2 volumes of nitrogen. This shows that the ratio of atoms of nitrogen to oxygen in the gas is 2 : 1. That the formula is N_2O, not N_4O_2, is decided by the specific gravity of the gas.

When a known volume of nitric oxide is passed over a weighed quantity of red-hot copper and the nitrogen which passes on is collected and measured, it is found that for every 16 parts by weight of oxygen absorbed by the copper (judged from its gain of weight) 11.11 litres of nitrogen are collected; but this volume of nitrogen weighs 14 grams (p. 47), so that the nitric oxide must contain O : N = 16 : 14, or one atom of oxygen to one atom of nitrogen. That the formula is NO, not N_2O_2, follows from the specific gravity of the gas.

The other oxides of nitrogen are similarly analysed.

67. **Reduction products of nitric acid.**—By the action of nascent hydrogen, that is, hydrogen at the moment of its liberation,* nitric acid, the most highly oxidised nitrogen compound, may be made to yield successive reduction products until the most highly hydrogenised nitrogen compound, ammonia, is formed. The reduction may be regarded as occurring in the following stages, although to realise such progressive steps is difficult, if not impossible, in practice. The first stage of the reduction will be nitrous acid, $NO_2{\cdot}OH + H_2 = NO{\cdot}OH + H_2O$. In the second stage, N·OH would be expected to be produced, but in a compound of this formula only one of the atom-linking powers

* When it might be supposed to be still in the condition of free atoms, and therefore more active. The usual method of applying nascent hydrogen is to liberate it in the liquid on which it is to act by placing zinc and sulphuric acid, or merely sodium amalgam, therein.

of the nitrogen would be satisfied; hence this group of atoms is incapable of a separate existence, but, if produced, immediately combines with a like group, forming *hyponitrous acid*, HO·N : N·OH. The third stage of the reduction consists in the introduction of hydrogen into the hyponitrous acid, whereby the molecule is made to yield either two molecules of a compound called *hydroxylamine*, HO·N : N·OH + H_4 = HO·N<(H H / H H)>N·OH, or one molecule of a compound called *hydrazine*, HO·N : N·OH + H_6 = H_2N : NH_2 + 2HOH. The final stage of the reduction transforms the hydroxylamine into ammonia.

Hyponitrous acid, $H_2N_2O_2$. Nitrous oxide might be expected to be the anhydride of this acid, $N_2O + H_2O = H_2N_2O_2$, but an aqueous solution of this gas does not contain hyponitrous acid. The hyponitrites are obtained by reducing solutions of the nitrates or nitrites by the nascent hydrogen generated when sodium amalgam is introduced into the solution. Thus, a solution of sodium hyponitrite is obtained when sodium amalgam is added, little by little, to a strong solution of sodium nitrate, or nitrite, kept cool. The hyponitrite most easily obtained in a pure condition is the silver salt, $Ag_2N_2O_2$, which is thrown down as a yellow precipitate when silver nitrate is added to the solution of sodium hyponitrite. The yellow precipitate dissolves in ammonia and in dilute nitric acid, but is precipitated unchanged by neutralising the solvent; it is insoluble in acetic acid. By adding hydrochloric acid to the silver salt, hyponitrous acid passes into the solution and silver chloride remains undissolved; the solution is colourless and acid to litmus, but it will not liberate carbon dioxide from the alkali carbonates; when kept it decomposes with formation of N_2O and H_2O. By adding the silver salt to a solution of HCl in ether, filtering and evaporating the ethereal solution, crystals of $H_2N_2O_2$ are obtained; they are very explosive, like other compounds containing the group ·N : N·. In acid solution potassium permanganate oxidises hyponitrous acid to nitric acid, but in alkaline solution a nitrite is formed. The formation of hyponitrous acid by the reduction of nitric oxide in presence of water has been mentioned at p. 98; another reaction by which it is produced will be mentioned below.

Hydroxylamine, NH_2·OH, may be obtained by the reduction of nitric acid, but is better prepared by passing nitric oxide through a series of flasks containing tin and strong hydrochloric acid. The hydrogen evolved from the metal and acid (the evolution is generally hastened by the addition of a few drops of platinic chloride, the platinum of which deposits on the tin and forms a galvanic couple) may be regarded as converting the NO into NH_2OH. The hydroxylamine, being possessed of basic properties, combines with the hydrochloric acid and remains in the solution as *hydroxylamine hydrochloride*, $NH_2OH.HCl$, together with stannous chloride. The tin is precipitated by the addition of H_2S; the SnS is filtered off and the filtrate evaporated, when the hydroxylamine hydrochloride crystallises.

To obtain free hydroxylamine, the hydrochloride is dissolved in methyl alcohol and a solution of sodium in the same solvent is added; sodium chloride is precipitated and is filtered off; the filtrate is then distilled under reduced pressure, when methyl alcohol passes over, followed by hydroxylamine. In this process the sodium methoxide, CH_3ONa, contained in the solution of sodium in methyl alcohol, reacts with the hydroxylamine hydrochloride, forming sodium chloride, hydroxylamine and methyl alcohol: $NH_2.OH.HCl + CH_3ONa = NH_2OH + CH_3OH + NaCl$. Sodium hydroxide cannot be substituted for the methoxide because water would be one of the products, and this decomposes the hydroxylamine.

Hydroxylamine crystallises in white needles, melts at 33° C., and boils at 58° C. under 22 mm. pressure, but explodes when heated to 90° C. under ordinary pressure. It is odourless and has an alkaline reaction; when exposed to air it deliquesces and ultimately evaporates; even in sealed tubes it slowly undergoes decomposition.

Hydroxylamine and its salts are very easily oxidised to nitrous oxide and water so that they reduce cupric oxide in alkaline solutions to cuprous oxide, $4CuO + 2NH_2.OH = 2Cu_2O + N_2O + 3H_2O$. Ferrous hydroxide, however, is oxidised by hydroxylamine, which is thereby reduced to ammonia; on the other hand, an acid

ferric solution is reduced by hydroxylamine. An aqueous solution of the hydrochloride is used as a photographic developer.

The free base combines with many metallic salts in the same way that water and ammonia do.

If hydroxylamine be regarded as formed on the type of water, it will be seen to contain the radicle NH_2 in place of H in H.OH. Equally well it may be said to be ammonia in which one hydrogen atom has been exchanged for OH. Before hydroxylamine was known, it could be prophesied that such a compound would be more basic than is water, and less basic than is ammonia. For it is found that the presence of an NH_2 group in a compound tends to make that compound basic, whilst the presence of an OH group tends to make it acid. Thus the basic properties of NH_2H are enfeebled by the substitution of an OH group for H.

The acid properties of $NO_2.OH$ are stronger than those of NO.OH, which in their turn are stronger than those of HO.N : N.OH. It would thus seem that NO_2 is a stronger acid radicle than NO, and that the two hydroxyl groups in hyponitrous acid do not compensate in acid-producing power for the absence of an oxy-nitrogen group.

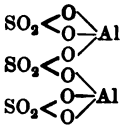
Since there are two OH groups in hyponitrous acid, this is a dibasic acid, that is to say, it contains two hydrogen atoms which can be displaced by metals.

Classification of acids.—*Acids are classified* into *monobasic*, *dibasic*, *tribasic*, and *tetrabasic* according as they have one, two, three, or four hydroxyl groups. Nitric acid is monobasic; $NO_2.OH$. Sulphuric acid is dibasic; $SO_2(OH)_2$. Phosphoric acid is tribasic; $PO(OH)_3$. Silicic acid is tetrabasic; $Si(OH)_4$.

On considering these formulæ it will be apparent that since – OH is a monovalent radicle $(NO_2)^{I}$ is a monovalent radicle, for it combines with only one OH. Similarly, $(SO_2)^{II}$ is a divalent radicle, $(PO)^{III}$ a trivalent, and $(Si)^{IV}$ a tretravalent radicle.

Normal salts are those in which all the H of the hydroxyl groups is exchanged for metal, as, for instance, in normal potassium sulphate $SO_2(OK)_2$, normal sodium phosphate $P(ONa)_3$. *Acid salts* are those in which only part of the hydrogen has been exchanged for the metal, as, for instance, acid potassium sulphate, $SO_2OH.OK$, diacid sodium phosphate, $PO(OH)_2(ONa)$.

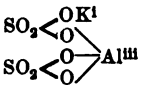
In forming a normal salt from a divalent metal, like calcium, and a monobasic acid, like nitric acid, it is necessary to have two molecules of the acid in order to obtain sufficient hydrogen for the metal to displace; thus Ca will displace the H from $2(NO_2.OH)$ forming $\begin{matrix}NO_2.O\\NO_2.O\end{matrix}\!\!>$ Ca. The trivalent aluminium would require three molecules of nitric acid: $\begin{matrix}NO_2.O\\NO_2.O\\NO_2.O\end{matrix}\!\!>$Al. A similar process of counterbalancing occurs when a dibasic acid forms a normal salt with a trivalent element; thus, aluminium sulphate can only be formed from 2 atoms of Al^{III} and three molecules of H_2SO_4:



or $Al_2^{III}(SO_4)_3$.

Basic salts are generally composed of a normal salt and a hydroxide of the metal, as in basic bismuth nitrate $Bi(NO_3)_3.2Bi(OH)_3$.

Double salts are those in which the hydrogen of the hydroxyl has been exchanged for different metals, as in potassium-sodium carbonate $CO < \begin{matrix}ONa^{I}\\OK^{I}\end{matrix}$, potassium-aluminium sulphate



Equivalents of acids and bases.—When a metal is substituted for half the hydrogen in water the compound is a hydroxide, *e.g.*, sodium hydroxide $Na^{I}OH$; calcium hydroxide $Ca^{II}<^{OH}_{OH}$, aluminium hydroxide Al^{III} When both atoms of hydrogen in water are exchanged for metal an oxide of the metal is produced NaONa, or Na_2O, Ca Ca, or CaO, Al Al, or Al_2O_3.

When a base neutralises an acid, a salt is formed, a base being either the oxide or the hydroxide of a metal. Thus the three bases, potash (KOH), soda (NaOH), and lime (CaO), neutralise nitric acid in accordance with the equations:

$$\underset{56}{KOH} + \underset{63}{HNO_3} = KNO_3 + H_2O\,;\quad \underset{40}{NaOH} + \underset{63}{HNO_3} = NaNO_3 + H_2O:$$

$$\underset{56}{CaO} + \underset{126}{2HNO_3} = Ca(NO_3)_2 + H_2O.$$

From these equations it is seen that 56 parts of KOH, 40 parts of NaOH, and 28 parts of CaO are required, respectively, to neutralise 63 parts of nitric acid. Consequently these proportions of these bases are equivalent to each other in neutralising power, and this will hold good towards other acids than nitric acid, thus it will be found that 112 parts of KOH are required to neutralise 98 parts of H_2SO_4, and that 80 parts of NaOH and 56 parts of CaO will suffice for the same purpose, the ratio being 56 : 40 : 28, as before.

The *equivalent of a base* is the number of grams of it which will neutralise one gram-molecule of a monobasic acid.

Again, if the quantity of different acids required to neutralise a given weight of a base be compared, the ratio between the quantities will be found to be constant for every base. Thus 63 parts of nitric acid, 49 parts of sulphuric acid, and $32\frac{2}{3}$ parts of phosphoric acid are required respectively to neutralise 56 parts by weight of potash. These quantities of these acids are therefore equivalent to each other in neutralising power; and moreover the same ratio will be found to hold when the acids are used to neutralise 40 parts of NaOH or 56 parts of CaO.

The *equivalent of an acid* is the number of grams of it which will neutralise one gram-molecule of potash or soda.

It will be obvious that when a table of equivalents is constructed the quantity of any acid which must be added to any base to form a neutral salt can be seen at a glance, for this quantity is the equivalent of the acid and of the base respectively.

For the hydrogen of ammonia there may be substituted potassium, sodium, and a few other metals having a high affinity for oxygen. Thus by passing dry ammonia over gently heated sodium, *sodamide*, $NaNH_2$, is formed; *potassamide*, KNH_2, is similarly prepared. These are white waxy substances which melt (at 155° and 270° C. respectively) to greenish liquids and partly sublime; at a red heat they are converted into their elements. Water immediately decomposes them, yielding NaOH, or KOH and NH_3.

Compounds containing the *amidogen* group (NH_2) are called *amides*. When nitrous acid is brought in contact with an amide at the ordinary temperature (in aqueous solution), the amidogen group is exchanged for the hydroxyl of the nitrous acid, and the NH_2 thus removed reacts with the NO of the acid to form N_2 and H_2O. Thus the simplest amide, hydrogen amide or ammonia $NH_2{\cdot}H$, reacts with nitrous acid to form hydrogen hydroxyl or water: $NH_2{\cdot}H + NO{\cdot}OH = HO{\cdot}H + N_2 + H{\cdot}OH$. This reaction is typical of one which is very commonly employed in organic chemistry for substituting OH for NH_2. When

it is applied to hydroxylamine, or hydroxyl-amide, $NH_2 \cdot OH$, it does not occur on exactly the same lines, possibly because hydroxyl-hydroxyl, or hydrogen dioxide, $HO \cdot OH$, which would be the product, is too unstable to be formed under the circumstances. The actual reaction between nitrous acid and hydroxylamine at ordinary temperatures may be represented by the equation $NH_2 \cdot OH + NO \cdot OH = HOH + N_2O + HOH$. Since nitrous acid cannot be preserved in aqueous solution its application for such reactions is effected by generating it at the moment when it is required by dissolving sodium nitrite in the solution to be treated, and adding an acid to liberate nitrous acid from the nitrite.

In the case of a large number of amides, particularly those derived from organic compounds, when the aqueous solution of the amide is kept cool by ice, no nitrogen is evolved on the addition of nitrous acid. This is because the nitrogen of the amidogen and of the nitrous acid remain combined together to form a group, $\cdot N : N \cdot$, in which each nitrogen atom is able to attach to itself a monovalent element or radicle. Such a nitrogen group is called a *diazo-group*, and compounds containing it are called *diazo*-compounds. To exemplify the *diazo-reaction* the following hypothetical equation for the reaction of ammonia on nitrous acid at a low temperature may be written: $H \cdot NH_2 + NO \cdot OH = HN : N \cdot OH + HOH$. The diazo-compound represented by the formula $HN : N \cdot OH$ has not been obtained, but it will be seen that hyponitrous acid may be regarded as formed on this type, HO being exchanged for the left-hand hydrogen atom. A comparison of the formula for hydroxylamine with that for ammonia will at once lead to the conclusion that the reaction between nitrous acid and hydroxylamine at a low temperature should produce hyponitrous acid; this is the case, for by mixing cold dilute solutions of hydroxylamine hydrochloride and sodium nitrite, sodium chloride and hydroxylamine nitrite are formed, the latter immediately passing into hyponitrous acid; by adding acetic acid and silver nitrate the yellow silver hyponitrite is precipitated: (1) $HO \cdot NH_2, HCl + NaO \cdot NO = NaCl + HO \cdot NH_2, HO \cdot NO$; (2) $HO \cdot NH_2 + HO \cdot NO = HO \cdot N : N \cdot OH + HOH$. The diazo-compounds which contain hydroxyl readily decompose when the temperature is raised, the products of the decomposition being the same as those which result from the interaction of the original amide with nitrous acid at a high temperature. Thus, if the above experiment be conducted at a high temperature (above 50° C.) nitrous oxide is rapidly evolved, and no hyponitrous acid can be detected in the solution.

Hydrazine, N_2H_4.—It has already been pointed out that radicles are incapable of a separate existence; they can, however, unite with themselves to form compounds. From this point of view hydrogen dioxide is dihydroxyl $HO \cdot OH$. *Diamidogen* or *hydrazine*, $H_2N \cdot NH_2$, is another case of this kind; as noticed at p. 103, it is produced by the reduction of hyponitrous acid (sulphurous acid being the reducing agent), but this is not a convenient method for preparing it.

To prepare hydrazine, 30 grams of potassium diazomethanedisulphonate (*q. v.*) is added in fine powder to a solution made by first saturating a 20 per cent. solution of KOH with SO_2 and then adding 10 grams of KOH. The mixture is warmed until colourless, heated to boiling with 150 c.c. of dil. H_2SO_4 (1 : 5), filtered and cooled, whereupon *hydrazine sulphate*, $N_2H_4.H_2SO_4$ crystallises. The sulphate is dissolved in a very little water and mixed with the exact quantity of KOH to convert the H_2SO_4 into K_2SO_4, and with sufficient absolute alcohol to precipitate all the K_2SO_4.

After filtration the alcohol is distilled and the temperature is raised to 115° C., whereupon *hydrazine hydrate*, N_2H_4,H_2O, distils. This is added to a retort containing BaO, heated for some hours at 110° C., and finally distilled under diminished pressure in a current of hydrogen. A large quantity of hydrazine sulphate must be used for a successful result.

Hydrazine is a colourless liquid of sp. gr. 1.013; it boils at 113.5° C. and melts at 1.4° C. It dissolves in water evolving much heat (37,800 cals. per gram-molecule), forming a hydrate $N_2H_4,2H_2O$ which passes into N_2H_4,H_2O if the water is evaporated. The latter hydrate is remarkably stable, resembling the caustic alkalies in many respects but of even more caustic properties; it is a colourless fuming liquid of sp. gr. 1·03, melts at −40° C. and boils at 120° C. It is powerfully alkaline and corrodes cork, rubber, and even glass when heated, so that these materials must be avoided in its manufacture; hydrazine itself, however, does not attack glass. With acids hydrazine hydrate yields two classes of salts, *e.g.*, N_2H_4,HCl and $N_2H_4,2HCl$; those with one molecular proportion of acid are the more stable.

Hydrazine and its compounds are powerful reducing agents.

Hydrogen nitride, azoimide, hydrazoic acid, or *hydronitrous acid*.—When hydrazine hydrate is treated with nitrous acid in a cooled dilute solution it is converted into *hydrogen nitride*, $\overset{N}{\overset{\|}{N}}\!>\!NH$; $H_2N\cdot NH_2 + NO\cdot OH = \overset{N}{\overset{\|}{N}}\!>\!NH + 2HOH$.

This compound is a colourless liquid (b.p. 37° C.), characterised by its explosiveness and its foul odour. It is distinguished from the other compounds of nitrogen with hydrogen by its acid properties. It dissolves many metals with evolution of hydrogen and production of metallic *nitrides*, such as $Zn^{II}(N_3)_2$. It has been sought to explain these acid properties by regarding hydrogen nitride as a nitric acid derivative, the nitrogen of which might be supposed to retain an acid bias. It is noticeable that most nitrogen compounds in which the nitrogen is not present as NH_2, or an equivalent group, have an acid character.

Hydrogen nitride is only obtained in small quantity by the above reaction. It is most conveniently prepared by the interaction between sodamide and nitrous oxide, sodium nitride, from which the free acid can be obtained, being produced; $NH_2Na + N_2O = N_3Na + H_2O$. Sodium is gently heated in a porcelain boat contained in a combustion tube through which dry ammonia is passed; when the metal has been completely converted into sodamide, a current of dry N_2O is substituted for the NH_3, the temperature being raised to about 200° C. The sodium nitride is transferred to a flask and distilled with dilute sulphuric acid. To the dilute solution of N_3H which distils over silver nitrate is added, whereby silver nitride N_3Ag is precipitated in a white crystalline form. This is washed and distilled with dilute H_2SO_4. A solution containing 27 per cent. of N_3H is thus obtained; it is fractionally distilled, and the first fraction is dried over calcium chloride and redistilled. The 27 per cent. solution is a slightly viscid liquid, specifically heavier than water; it evolves N_3H at the ordinary temperature, and the vapour gives thick clouds when in contact with ammonia. The acid corrodes the skin and produces giddiness and headache when inhaled. Most of the salts crystallise well, those of silver and mercurous mercury being insoluble; they are all explosive, except those of the alkali metals.

There is a remarkable similarity between hydrazoic acid and hydrochloric acid, extending even to their salts which resemble each other in solubility and crystalline form; indeed, in the case of sodium nitride the resemblance extends to the salt taste.

Silver nitride may conveniently be obtained by cautiously warming 1.5 gram of hydrazine sulphate with 4 c.c. of nitric acid of sp. gr. 1 3 and passing the N_3H which is evolved into a solution of $AgNO_3$.

CARBON.

C = 12 parts by weight.*

68. This element is especially remarkable for its uniform presence in organic substances. The ordinary laboratory test by which the chemist decides whether a substance under examination is of organic origin, consists in heating it with limited access of air, and observing whether any blackening from separation of carbon (*carbonisation*) ensues.

Few elements are capable of assuming so many different aspects as is carbon. It is met with transparent and colourless in the *diamond*, opaque, black, and quasi-metallic in *graphite* or black lead, dull and porous in wood *charcoal*, and under new conditions in *anthracite*, *coke*, and *gas-carbon*.

In nature, free carbon may be said to occur in the forms of diamond, graphite, and anthracite (the other varieties of coal containing considerable proportions of other elements).

Apart from its great beauty and rarity, the diamond possesses a special interest in chemical eyes, from its having perplexed philosophers up to the middle of the last century, notwithstanding the simplicity of the experiments required to demonstrate its true nature. The first idea of it appears to have been obtained by Newton, when he perceived its great power of refracting light, and thence inferred that, like other bodies possessing that property in a high degree, it would prove to be combustible ("an unctuous substance coagulated"). When the prediction was verified, the burning of diamonds was exhibited as a marvellous experiment, but no accurate observations appear to have been made till 1772, when Lavoisier ascertained, by burning diamonds suspended in the focus of a burning-glass in a confined portion of oxygen, that they were entirely converted into carbonic acid gas. In more recent times this experiment has been repeated with the utmost precaution, and the diamond has been clearly demonstrated to consist of carbon in a crystallised state.

A still more important result of this experiment was the exact determination of the composition of carbon dioxide, without which it would not be possible to ascertain exactly the proportion of carbon in any of its numerous compounds, since it is always weighed in that form.

The classical experiments upon the synthesis of carbon dioxide were conducted with the arrangement represented in Fig. 81.

Within a porcelain tube A, which is heated to redness in a charcoal fire, was placed a little platinum tray, accurately weighed, and containing a weighed quantity of fragments of diamond. One end of the tube was connected with a gas-holder B, containing oxygen, which was thoroughly purified by passing through the tube C, containing potash (to absorb any carbonic acid gas and chlorine which it might contain), and dried by passing over pumice soaked with concentrated sulphuric acid in D and E. To the other end of the porcelain tube A, there was attached a glass tube F, also heated in a furnace, and containing oxide of copper to convert into carbon dioxide (CO_2) gas any carbon monoxide (CO) which might have been formed in the combustion of the diamond. The CO_2 was then passed over pumice soaked with sulphuric acid in G, to remove any traces of moisture, and afterwards into a weighed bulb-apparatus H, containing solution of potash, and two weighed tubes I, K, containing, respectively, solid potash and sulphuric acid on pumice, to guard against the escape of aqueous vapour taken up by the excess of oxygen in its passage through the bulbs H. The increase of weight in H, I, K, represented the

* Inasmuch as carbon is non-volatile, the volume occupied by one atomic weight of it is not known.

CO_2 formed in the combustion of an amount of diamond indicated by the loss of weight suffered by the platinum tray, and the difference between the diamond consumed and the CO_2 formed would express the amount of oxygen which had combined with the carbon. A large number of experiments conducted in this manner,

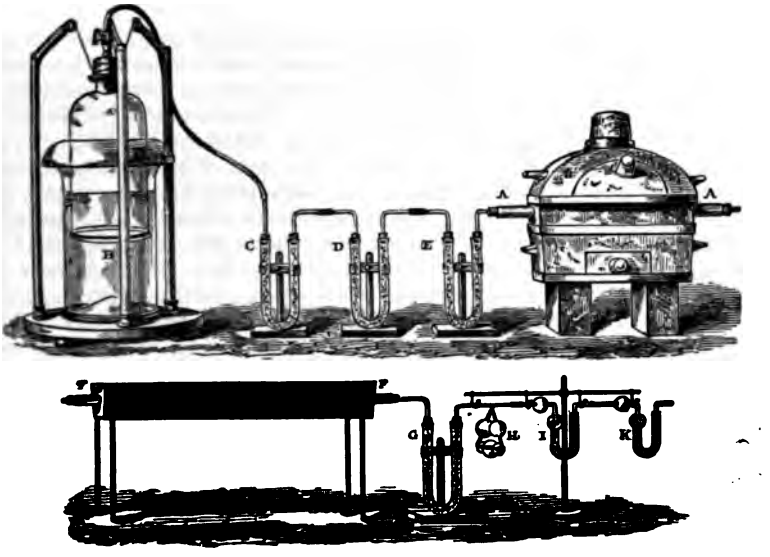


Fig. 81.—Exact synthesis of carbonic acid gas.

both with diamond and graphite, showed that 12 parts of carbon furnished 44 parts of CO_2, and consumed, therefore, 32 parts of oxygen.

A convenient arrangement for burning a diamond in oxygen is shown in Fig. 82. The diamond is supported in a short helix of platinum wire A, which is attached to the copper wires B B, passing through the cork C, and connected with the terminal wires of a Grove's battery of five or six cells. The globe having been filled with oxygen by passing the gas down into it till a match indicates that the excess of oxygen is streaming out of the globe, the cork is inserted, and the wires connected with the battery. When the heat developed in the platinum coil by the passage of the current, has raised the diamond to a full red heat, the connection with the battery may be interrupted, and the diamond will continue to burn with steady and intense brilliancy.

Fig. 82.

To an observer unacquainted with the satisfactory nature of this demonstration, it would appear incredible that the transparent diamond, so resplendent as to have been reputed to emit light, should be identical in its chemical composition with graphite (*plumbago* or *black lead*), from which, in external appearance, it differs so widely. For this difference is not confined to their colour; in crystalline form they are not in the least alike, the diamond occurring generally in octahedral crystals, whilst graphite is found either in *amorphous* masses (that is, having no definite crystalline form), or in six-sided plates which are not geometrically allied with the form assumed by the diamond. Carbon, therefore, is *dimorphous*, or occurs in two distinct crystalline forms. Even in weight, diamond and graphite are very dissimilar, the former having an average specific gravity of 3.5 and the latter of 2.3. Again,

a crystal of diamond is the hardest of all substances, whence it is used for cutting and for writing upon glass, but a mass of graphite is soft and easily cut with a knife. The diamond is a non-conductor of electricity, but the conducting power of graphite renders it useful in the electrotype process.

Diamonds are chiefly obtained from Golconda, Borneo, Kimberley in South Africa, and the Brazils. They usually occur in sandstone rock or in mica slate. The hardness of the diamond renders it necessary to employ diamond-dust for the purpose of cutting and polishing it, which is effected with the aid of a revolving disc of steel, to the surface of which the diamond-dust is applied in the form of a paste made with oil. The crystal in its natural state is best fitted for the purpose of the glazier, for its edges are usually somewhat curved, and the angle formed by these cuts the glass deeply, while the angle formed by straight edges, like those of an ordinary jeweller's diamond, is only adapted for scratching or writing upon glass. Drills with diamond points have been employed in tunnelling through hard rocks. The diamond-dust used for polishing, &c., is obtained from a dark amorphous diamond (*Carbonado*) found at Bahia in the Brazils; 1000 ounces annually are said to have been occasionally obtained from this source. When burnt, the diamond always leaves a minute proportion of ash of a yellowish colour in which silica and oxide of iron have been detected. A genuine diamond may be known by its combining the three qualities of extreme hardness, enabling it to scratch hardened steel, high specific gravity (3.52), and insolubility in hydrofluoric acid.* Sapphire (Al_2O_3) is nearly as hard as diamond, but its specific gravity is about 4.

Although the diamond, when preserved from contact with the air, may be heated very strongly in a furnace, without suffering any change, it is not proof against the intense heat of the discharge taking place between two carbon points attached to the terminal wires of a powerful galvanic battery. If the experiment be performed in a vessel exhausted of air, the diamond becomes converted into a black coke-like mass which closely resembles graphite in its properties.

Graphite always leaves more ash than the diamond, consisting chiefly of the oxides of iron and manganese, with particles of quartz, and sometimes titanic oxide. The purest specimens are those of compact amorphous graphite from Borrowdale in Cumberland; an inferior variety, imported from Ceylon, is crystalline, being composed of hexagonal plates. Graphite is obtained artificially in the manufacture of cast iron: in some cases, a portion of the carbon of the cast iron separates in cooling, in the form of crystalline scales of graphite, technically called *kish*. In the grey variety of cast iron these scales of graphite are diffused through the mass of the metal, and are left undissolved when the iron is dissolved by an acid.

Graphite is far more useful than the diamond, for, in addition to its application in black-lead pencils, and for covering the surface of iron in order to protect it from rust, it is largely employed, in admixture with

* Artificial diamonds have been made by dissolving amorphous carbon in molten iron heated to nearly 3000° C. in the electric furnace, and suddenly cooling the metal by pouring it into molten lead. In this way only the surface of the globules of iron is immediately solidified. The interior expands as it cools and creates that pressure on the carbon it contains, which appears to be essential to the formation of diamond. By dissolving the iron in acids the diamonds are left. They are never comparable with the natural product.

clay, for the fabrication of the plumbago crucibles (*blue pots*), which are so valuable to the metallurgist for their power of resisting high temperatures and sudden change of temperature. Graphite is also sometimes employed for lubricating, to diminish friction in machinery, and for *facing* or imparting a glazed surface to gunpowder.

Inferior kinds of graphite are treated by *Brodie's* process. The graphite is heated with 2 parts of sulphuric acid and $\frac{1}{4}$th or $\frac{1}{5}$th of potassium chlorate. A part of the graphite is thus oxidised and converted into *graphitic acid*, $C_{11}H_4O_5$. When the graphite so treated is washed, dried, and heated to redness, the graphitic acid is decomposed, evolving steam and carbonic oxide gas, which swells up the graphite to a light voluminous powder which can be separated from the heavy earthy impurities by floating it in water. When much silica is present in the graphite, a little sodium fluoride is added after the potassium chlorate has been decomposed.

(Anthracite and the other varieties of coal will be described in a separate section.)

69. Several varieties of carbon ("pseudo-carbons"), obtained by artificial processes, are employed in the arts. The most important of these are *lamp black*, *wood charcoal*, and *animal charcoal*.

Lamp black approaches more nearly in composition to pure carbon than either of the others, and is the soot obtained from the imperfect combustion of resinous and tarry matters (or of highly bituminous coal), from which source it derives the small quantities of resin, nitrogen, and sulphur which it contains. The uses of this substance, as an ingredient of pigments, of printing-ink, and of blacking, depend evidently more upon its black colour than upon its chemical properties. *Diamond black* is a very pure variety of lamp black obtained by the imperfect combustion of the natural hydrocarbon gas of the Ohio petroleum region. *Spanish black* is charcoal made from waste cork.

Wood charcoal presents more features which arrest the attention of the chemist, as well on account of its specific properties as of the influence exercised by the method adopted for obtaining it, upon its fitness for the particular purpose which it may be destined to serve.

If a piece of wood be heated in an ordinary fire, it is speedily consumed, with the exception of a grey ash consisting of the incombustible mineral substances which it contained; if the experiment were performed in such a manner that the products of combustion of the wood could be collected, these would be found to consist of carbonic acid gas and water; woody fibre is composed of carbon, hydrogen, and oxygen in the proportion represented by the formula $C_6H_{10}O_5$, and when it is burnt, the oxygen, in conjunction with more oxygen derived from the air, converts the carbon and hydrogen into carbon dioxide and water. But if the wood be heated in a glass tube, closed at one end, it will be found impossible to reduce it, as before, to an ash, for a mass of charcoal will remain, having the same form as that of the piece of wood; in this case, the oxygen of the air not having been allowed free access to the wood, no true combustion has occurred, but the wood has undergone *destructive distillation*, that is, its elements have arranged themselves, under the influence of the high temperature, into different forms of combination, for the most part simpler in their chemical composition than the wood itself, and capable, unlike the wood, of enduring that temperature without decomposition; thus, it is merely an exchange of

an unstable for a stable equilibrium of the particles of matte posing the wood.

(DEFINITION.—*Destructive distillation* is the resolution of a c substance into simpler vapours and gases under the influence c out of contact with air.)

The vapours issuing from the mouth of the tube will be fou to blue litmus-paper; they have a peculiar odour, and readily t on contact with flame. These will be more particularly notice after, as they contain some very useful substances. The charcoa is left is not pure carbon, but contains considerable quantities of and hydrogen with a little nitrogen, and the mineral matter or the wood.

When the charcoal is to be used for fuel, it is generally prep a process in which the heat developed by the combustion of a of the wood is made t the charring of the rest this view the billets o are built up into a (Fig. 83) around stakes into the ground, a being left so that th may be kindled in the This mound of wood, is generally from 30 feet in diameter, is

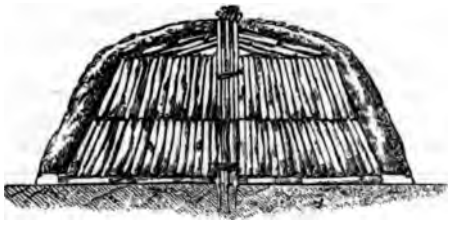


Fig. 83.—Charcoal heap.

covered with turf and sand, except for a few inches around th where it is left uncovered to give vent to the vapour of water e from the wood in the first stage of the process. When the he been kindled in the centre, the passage left for this purpose is ca closed up. After the combustion has proceeded for some time, is judged that the wood is perfectly dried, the open space at t is also closed, and th left to smoulder for t four weeks, when the perfectly carbonised.

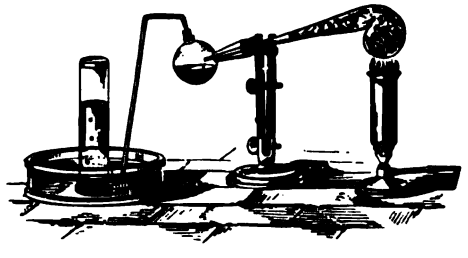


Fig. 84.—Distillation of wood.

Upon an average, 2 of charcoal are obtai this process from wood.

On the small sca operation may be co in a glass retort, as sh Fig. 84, where the wat and naphtha are deposited in the globular receiver, and the inflar gases are collected over water.

During the destructive distillation the hydrogen and oxygen wood are for the most part expelled in the forms of wood n (CH_4O), pyroligneous acid ($C_2H_4O_2$), carbon dioxide, carbon mo water, &c., leaving a residue containing a much larger propor carbon than that contained by the original wood.

Much attention has been paid to the manufacture of charcoal for gunp mixture of charcoal, sulphur, and saltpetre), and it has been found that th

the temperature to which the charcoal is exposed in its preparation, the larger the proportion of hydrogen and oxygen expelled, and the more nearly does the charcoal approach in composition to pure carbon; but it is not found advantageous in practice to employ so high a temperature, since it yields a dense charcoal of difficult combustibility, and therefore less fitted for the manufacture of powder. The average composition of wood, exclusive of ash, is, in 100 parts—50 parts carbon, 6 parts hydrogen, and 44 parts oxygen.

The composition of the charcoal prepared at different temperatures is given in the following table:

Temperature of Charring.	Carbon.	Hydrogen.	Oxygen.	Ash.
270° C.	71.0	4.60	23.00	1.40
363°	80.1	3.71	14.55	1.64
476°	85.8	3.13	9.47	1.60
519°	86.2	3.11	9.11	1.58

The charcoal employed for black gunpowder in this country is prepared at temperatures between 360° C. and 520° C. It will be seen that the proportion of carbon, upon which the heating value of the charcoal depends, increases with the final temperature of carbonisation; but it has been found that the rapidity with which the temperature is raised has also a great effect in increasing the proportion of carbon, as shown in the following table:

Final Temperature.	Time of Heating.	Percentage of Carbon.	Final Temperature.	Time of Heating.	Percentage of Carbon.
410° C.	5 hours	81.65	490° C.	2¾ hours	86.34
414°	2¾ ,,	83.14	555°	3⅜ ,,	83.32
490°	3¼ ,,	84.19	558°	3 ,,	86.52

The charcoal prepared between 260° and 320° C. has a brown colour (*charbon roux*), and since it is more easily inflamed than the black charcoal obtained at higher temperatures, it is used in powders where the proportion of sulphur is reduced. It is prepared by exposing the wood, in an iron cylinder, to the action of high pressure steam heated to about 280° C. Charcoal prepared at low temperatures gives somewhat higher velocities to gunpowder in which it is used, but absorbs much more moisture than that prepared at high temperatures.

Light woods, such as alder, willow, and dogwood,* are selected for the preparation of charcoal for gunpowder, because they yield a lighter and more easily combustible charcoal, dogwood being employed for the best quality of powder for small arms. This wood is chiefly imported, since it has not been successfully grown in this country. It is stripped of its bark, and either exposed for a length of time to the air or dried in a hot chamber. Considerable loss of charcoal occurs if damp wood be charred, a portion of the carbon being oxidised by the steam at a high temperature.

In order to convert the wood into charcoal, 1½ cwt. of wood is packed into a sheet-iron cylinder or *slip* (Fig. 85), one end of which is closed by a tightly-fitting cover, and the other by a perforated plate, to allow of the escape of the gases and vapours expelled during the carbonisation. This cylinder is then introduced into a cylindrical cast-iron retort, built into a brick furnace, and provided with a pipe (L) for the escape of the products, which are usually carried back into the furnace (B) to be consumed. The process of charring occupies from 2½ to 3½ hours, and as soon as it is completed, which is known by the violet tint of the (carbonic oxide) flame

* Dogwood charcoal is not made from the true dogwood (*cornus*), but from the alder buckthorn (*Rhamnus frangula*), commonly called black dogwood.

from the pipe leading into the fire, the slip is transferred to an iron box or *extinguisher*, where the charcoal is allowed to cool. About 40 lbs. of charcoal are obtained from the above quantity of wood. Charcoal prepared by this process is spoken of as *cylinder charcoal*, to distinguish it from *pit charcoal*, prepared by the ordinary process of charcoal burning (Fig. 83), and used for fuse compositions, &c., but not for the best gunpowder. The fitness of the charcoal for the manufacture of powder is generally judged of by its physical characters. It is of course desirable that the charcoal should be as free from incombustible matter as possible. The proportion of the ash left by different charcoals varies considerably, but it seldom exceeds 2 per cent. This ash consists chiefly of the carbonates of potassium and calcium; it also contains calcium phosphate, magnesium carbonate, silicate and sulphate of potassium, chloride of sodium, and the oxides of iron and manganese.

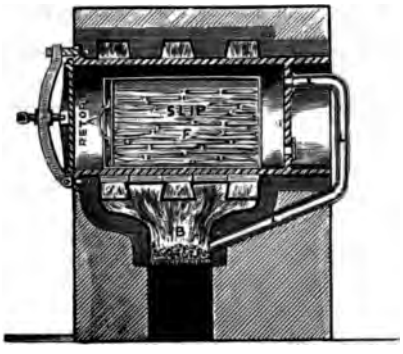


Fig. 85.—Charcoal retort.

The charcoal is kept for about a fortnight before being ground for making gunpowder, for if ground when fresh, before it has absorbed moisture and oxygen from the air, it is liable to spontaneous combustion.

The infusibility of the charcoal left by wood accounts for its very great porosity, upon which some of its most remarkable and useful properties depend. The application of charcoal for the purpose of "sweetening" fish and other food in a state of incipient putrefaction has long been practised, and more recently charcoal has been employed for *deodorising* all kinds of putrefying and offensive animal or vegetable matter. This property of charcoal depends upon its power of absorbing into its pores very considerable quantities of the gases, especially of those which are easily absorbed by water. Thus, 1 cubic inch of charcoal is capable of absorbing about 100 cubic inches of ammonia gas and 50 cubic inches of sulphuretted hydrogen, both which are conspicuous among the offensive results of putrefaction. This condensation of gases by charcoal is a mechanical effect, and does not involve a chemical combination of the charcoal with the gas; it is exhibited most powerfully by charcoal which has been recently heated to redness in a closed vessel, and cooled out of contact with air by plunging it under mercury. Eventually, the offensive gases absorbed by the charcoal are chemically acted on by the oxygen of the air in its pores. A cubic inch of wood charcoal absorbs nearly 10 cubic inches of oxygen, and when the charcoal containing the gas thus condensed is presented to another gas which is capable of undergoing oxidation, this latter gas is oxidised and converted into inodorous products. Thus, if charcoal be exposed to the action of air containing sulphuretted hydrogen gas (H_2S), it condenses within its pores both this gas and the atmospheric oxygen, which slowly converts the H_2S into sulphuric acid (H_2SO_4). The presence of so much air in charcoal renders it, like wood, apparently lighter than water; when powdered it sinks in water, its true specific gravity varying from 1.4 to 1.9.

The great porosity of wood charcoal is strikingly exhibited by attaching a piece of lead to a stick of charcoal (Fig. 86), so as to sink it in a cylinder of water, which is then placed under the receiver of the air-pump. On exhausting the air, innumer-

able bubbles will start from the pores of the charcoal, causing brisk effervescence. If a glass tube 16 or 18 inches long be thoroughly filled with ammonia gas (Fig. 87), supported in a trough containing mercury, and a small stick of recently calcined charcoal introduced through the mercury into the tube, the charcoal will absorb the ammonia so rapidly that the mercury will soon be forced up and fill the tube, carrying the charcoal up with it. On removing the charcoal and placing it upon the hand, a sensation of cold will be perceived from the rapid escape of ammonia, perceptible by its odour.

By exposing a fragment of recently calcined wood charcoal under a jar filled with hydrosulphuric acid gas for a few minutes, so that it may become saturated with the gas, and then covering it with a jar of oxygen, the latter gas will act upon the former with such energy that the charcoal will burst into vivid combustion. The jar must not be closed air-tight at the bottom, or the sudden expansion may burst it. Charcoal in powder exposed in a porcelain crucible may also be

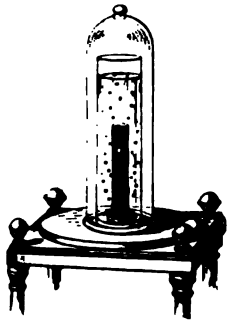


Fig. 86.

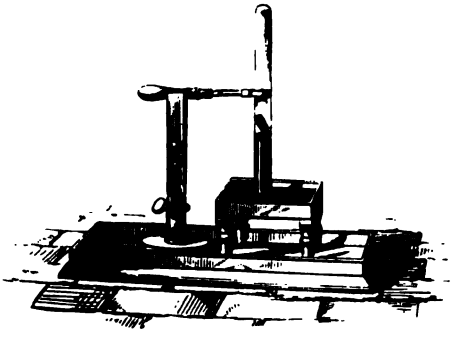


Fig. 87.

employed in the same way. It should be pretty strongly heated in the covered crucible, and allowed to become nearly cool before being exposed to the hydrosulphuric acid.

Charcoal prepared from hard woods absorbs the largest volume of gas. Thus charcoal made from the shell of the cocoa-nut will absorb 170 times its volume of ammonia gas and 18 times its volume of oxygen, although its pores are quite invisible, and its fracture exhibits a semi-metallic lustre.

As the gases which are evolved in putrefaction are of a poisonous character, the power of wood charcoal to remove them acquires great practical importance, and is applied in very many cases; the charcoal in coarse powder is thickly strewn over matters from which the effluvium proceeds, or is exposed in shallow trays to the air to be sweetened, as in the wards of hospitals, &c. It has even been placed in a flat box of wire gauze to be fixed as a ventilator before a window through which the contaminated air might have access, and respirators constructed on the same principle have been found to afford protection against poisonous gases and vapours. The ventilating openings of sewers in the streets may also be fitted with cases containing charcoal for the same purpose. Water is often filtered through charcoal in order to free it from the noxious and putrescent organic matters which it sometimes contains. For all such uses the charcoal should have been recently heated to redness in a covered vessel, in order to expel the moisture which it attracts when exposed to the air; and the charcoal which has lost its power of absorption will be found to regain it in great measure when heated to redness.

This power of absorption which charcoal possesses is not confined to

gases, for many liquid and solid substances are capable of being removed by that agent from their solution in water. This is most readily traced in the case of substances which impart a colour to the solution, such colour being often removed by the charcoal; if port wine or infusion of logwood be shaken with powdered charcoal (especially if the latter has been recently heated to redness in a closed crucible), the liquid, when filtered through blotting-paper, will be found to have lost its colour; the colouring-matter, however, seems merely to have adhered to the charcoal, for it may be extracted from the latter by treatment with a weak alkaline liquid.

The *decolorising power* of wood charcoal is very feeble in comparison with that possessed by *bone-black* or *animal charcoal*, which is obtained by heating bones in vessels from which the air is excluded. Bones are composed of about one-third of animal and two-thirds of mineral substances, the latter including calcium phosphate, which amounts to more than half the weight of the bone, and a little calcium carbonate. When bone is heated, as in a retort, so that air is not allowed to have free access to it, the animal matter undergoes destructive distillation, its elements—carbon, hydrogen, nitrogen, and oxygen—assuming other forms, the greater part of the last three elements, together with a portion of the carbon, escaping in different gaseous and vaporous products, while a considerable proportion of the carbon remains behind, intimately mixed with the earthly ingredients of the bone, and constituting the substance known as animal charcoal. The great difference between the products of the destructive distillation of bone and of wood deserves a passing notice. If a fragment of bone or a shaving of horn be heated in a glass tube closed at one end, the vapours which are evolved will be found strongly *alkaline* to test-papers, while those furnished by the wood were *acid*; this difference is to be ascribed mainly to the presence of nitrogen in the bone, wood being nearly free from that element; it will be found to hold good, as a general rule, that the results of the destructive distillation of animal and vegetable matters containing much nitrogen are alkaline, from the presence of ammonia (NH_3) and similar compounds, while those furnished by non-nitrogenised substances possess acid characters; the peculiar odour which is emitted by the heated bone is characteristic, and affords us a test by which to distinguish roughly between nitrogenised and non-nitrogenised bodies.

An examination of the charred mass remaining as the ultimate result of the action of heat upon bone, shows it to contain much less carbon than that furnished by wood, for the bone charcoal contains nearly nine-tenths of its weight of phosphate (with a little carbonate) of calcium; the consequence of the presence of so large an amount of earthy matter must be to extend the particles of carbon over a larger area, and thus to expose a greater surface for the adhesion of colouring-matters, &c. This may partly help to explain the very great superiority of bone-black to wood charcoal as a decolorising agent, and the explanation derives support from the circumstance, that when animal charcoal is deprived of its earthy matter, for chemical uses, by washing with hydrochloric acid, its decolorising power is very considerably reduced. The application of this variety of charcoal is not confined to the chemical laboratory, but extends to manufacturing processes. The sugar refiner

decolorises his syrup by filtering it through a layer of animal charcoal, and the distiller employs charcoal to remove the fusel oil with which distilled spirits are frequently contaminated.

Carbon is remarkable, among elementary bodies, for its indisposition to enter directly into combination with the other elements, whence it follows that most of the compounds of carbon have to be obtained by indirect processes. This element appears, indeed, to be incapable of uniting with any other at the ordinary temperature, and this circumstance is occasionally turned to useful account, as when the ends of wooden stakes are charred before being plunged into the earth, when the action of the atmospheric oxygen, which, in the presence of moisture, would be very active in effecting the decay of the wood, is resisted by the charcoal into which the external layer has been converted. The employment of black-lead to protect metallic surfaces from rust is another application of the same principle. At a high temperature, however, carbon combines readily with oxygen, sulphur, and with some of the metals, and, at a very high temperature, even with hydrogen and nitrogen. The tendency of carbon to combine with oxygen under the influence of heat, is shown when a piece of charcoal is strongly heated at one point, when the carbon at this point at once combines with the oxygen of the surrounding air (forming carbonic acid gas), and the heat developed by this combustion raises the neighbouring particles of carbon to the temperature at which the element unites with oxygen, and thus the combustion is gradually propagated throughout the mass, which is ultimately converted entirely into carbonic acid gas, nothing remaining but the white ash, composed of the mineral substances derived from the wood employed for preparing the charcoal. It is worthy of remark, that if charcoal had been a better conductor of heat, it would not have been so easily kindled, since the heat applied to any point of the mass would have been rapidly diffused over its whole bulk, and this point could not have attained the high temperature requisite for its ignition, until the whole mass had been heated nearly to the same degree; this is actually found to be the case in charcoal which has been very strongly heated (out of contact with air), when its conducting power is greatly improved and it kindles with very great difficulty. The ignition temperature of carbon (charcoal or coke) appears to be about 400° C. The *calorific value* of carbon in the form of wood charcoal is represented by the number 8080—that is, 1 gram of carbon, when burnt so as to form carbonic acid gas, is capable of raising 8080 grams of water from 0° C. to 1° C.

A given weight of charcoal will produce twice as much available heat as an equal weight of wood, since the former contains more actual fuel and less oxygen, and much of the heat evolved by the wood is absorbed or rendered latent in the steam and other vapours which are produced by the action of heat upon it. The attraction possessed by carbon for oxygen at a high temperature is turned to account in metallurgic operations, when coal and charcoal are employed for extracting the metals from their compounds with oxygen.*

The unchangeable solidity of carbon is another remarkable feature.

* Easily reducible oxides, such as oxide of lead, give carbon dioxide when heated with charcoal: $2PbO + C = Pb_2 + CO_2$, but oxides which are not easily reducible, such as oxide of zinc, give carbonic oxide: $ZnO + C = CO + Zn$.

Only at the temperature (3000° C.) attainable in the electric furnace can carbon be vaporised; even then it does not appear to pass through the liquid condition. Melted iron and some other fused metals dissolve carbon, but beyond these there is no solvent by the aid of which carbon may be brought into the liquid form by the process of solution; for although charcoal gradually disappears when boiled with sulphuric and nitric acids, it does not enter into simple solution, but is converted, as will be seen hereafter, into carbon dioxide.

The very striking difference in properties exhibited by diamond, graphite, and charcoal, lead to the belief that they consist of dissimilar carbon molecules. The investigation of the specific heats and other physical constants of these three varieties indicates that the diamond molecule contains more atoms than the graphite molecule contains, and that the charcoal molecule is still less complex.

When an element is capable of appearing in two or more forms, having different physical properties, these forms are said to be *allotropic*.

(DEFINITION.—*Allotropy* is the assumption of different properties without loss of chemical identity.)

Such cases, like those of *isomerism* among the compounds of carbon (see *Organic Chemistry*), will probably be explained by differences in the position and arrangement of the atoms in the molecule.

The specific heat of diamond increases with rise of temperature more rapidly than that of any other substance, ranging from 0.113 at 11° C. to 0.459 at 985° C. The specific heat of graphite at ordinary temperature is about 0.2. It is worthy of note that graphite is the final form of any kind of carbon which is submitted to a high temperature. Thus it is common to heat carbon rods or plates which are to be used as electrodes and must therefore have the best possible electrical conductivity and power of resisting chemical attack, to the highest attainable temperatures in order to "graphitise" them.

Pure carbon is prepared with some difficulty; the charcoal obtained by heating some pure organic substance containing C, H, and O, such as white sugar-candy, in a closed crucible, is heated in a porcelain tube, as strongly as possible, in a current of dry chlorine gas until no more HCl is produced. The residue in the tube is nearly pure carbon. The carbon deposited when acetylene is passed through a red hot tube is a very pure form.

70. Carbon is capable of combining with oxygen in two proportions, forming the compounds known as *carbonic oxide* or *carbon monoxide* (CO) and *carbon dioxide* (CO_2).

CARBON DIOXIDE OR CARBONIC ACID GAS.

$CO_2 = 44$ parts by weight $= 2$ volumes.

71. It has been already mentioned that carbonic acid gas is a component of the atmosphere, which usually contains about 3 volumes of carbonic acid gas in 10,000 volumes of air. The proportion is smaller at high altitudes. It is greater during the night than in the day, since plants only decompose carbon dioxide in daylight. The oleander leaf was found to decompose, on an average, in sunlight, 1108 cubic centimetres (67.6 cubic inches) of CO_2 per square metre (about 11 square feet) of leaf-surface, per hour.

The proportion of CO_2 does not vary materially in the neighbourhood of a town.

Carbonic acid gas is chiefly formed by the operation of the atmospheric oxygen in supporting combustion and respiration. All sub-

stances used as fuel contain a large proportion of carbon, which, in the act of combustion, combines with the oxygen, and escapes into the atmosphere in the form of carbonic acid gas. In the process of respiration, the carbonic acid gas is formed from the carbon contained in the blood and in the different portions of the animal frame to which oxygen is conveyed by the blood; the latter, in passing through the lungs, gives out, in exchange for the oxygen, a quantity of carbonic acid gas produced by the union of a former supply of oxygen with the carbon of the digested food, which has passed into the blood and has not been required for the repair of wasted tissue. This conversion of the carbon of the food into carbonic acid gas will be again referred to; it will be at once evident that it must be concerned in the maintenance of the animal heat.

The leaves of plants, under the influence of light, have the power of decomposing the carbon dioxide of the atmosphere, the carbon of which is applied to the production of vegetable compounds forming portions of the organism of the plant, and when this dies, the carbon is restored, after a lapse of time more or less considerable, to the atmosphere, in the same form, namely, that of carbon dioxide, in which it originally existed there. If a plant should have been consumed as food by animals, its carbon will have been eventually converted into carbonic acid gas by respiration; the use of the plant as fuel, either soon after its death (wood), or after the lapse of time has converted it into coal, will also consign its carbon to the air in the form of carbon dioxide. Even if the plant be left to *decay*, this process involves a slow conversion of its carbon into carbon dioxide by the oxygen of the air.

Putrefaction and fermentation are also very important processes concerned in restoring to the air, in the form of carbonic acid gas, the carbon contained in dead vegetable and animal matter. Although, in a popular sense, these two processes are distinct, yet their chemical operation is of the same kind, consisting in *the resolution of a complex substance into simpler forms, produced by contact with some minute living plant or animal.* The discussion of the true nature of the process (which is even now somewhat obscure) would be premature at this stage, and it will suffice for the present to state that carbonic acid gas is one of the simpler forms into which the carbon is converted by the metamorphosis which ensues so quickly upon the death of animals and vegetables.

Fig. 88.

The production of carbon dioxide in combustion, respiration, and fermentation, may be very easily proved by experiment. If a dry bottle be placed over a burning wax taper standing on the table, the sides of the bottle will be covered with dew from the combustion of the hydrogen in the wax; and if a little clear lime-water be shaken in the bottle, the milky deposit of calcium carbonate will indicate the formation of carbon dioxide.

By arranging two bottles, as represented in Fig. 88, and inspiring through the tube A, air will bubble through the lime-water in B, before entering the lungs, and will then be found to contain too little carbon dioxide to produce a milkiness, but on expiring the air, it will bubble through C, and will render the lime-water in this bottle very distinctly turbid.

If a little sugar be dissolved in eight or ten times its weight of warm (not hot) water, in a flask provided with a cork and delivery tube and a little dried yeast, previously rubbed down with water, added, fermentation will begin in the course of an hour or less, and carbonic acid gas may be collected in a jar standing in a pneumatic trough.

72. In the mineral kingdom, carbon dioxide is pretty abundant. The gas issues from the earth in some places in considerable quantity, as at Nauheim, where there is said to be a spring exhaling about 1,000,000 lbs. of the gas annually. Many spring waters, those of Seltzer and Pyrmont, for example, are very highly charged with the gas.

Carbon dioxide is found in the air of soils in larger proportion than in the atmosphere, amounting to 20 or 30, and occasionally even to 600, vols. in 10,000. It increases with the temperature, and originates from the decay of vegetable matter.

But it occurs in far larger quantity in the immense deposits of *limestone*, *marble*, and *chalk*, which compose so large a portion of the crust of the globe. Calcium carbonate is also met with in the animal kingdom. Oyster-shells contain 98 per cent. and egg-shells 97 per cent. of it, and pearls contain about two-thirds of their weight.

The expulsion of the carbonic acid gas from limestone ($CaCO_3$) forms the object of the process of *lime burning*, by which the large supply of lime (CaO) is obtained for building and other purposes. But if it be required to obtain the carbonic acid gas without regard to the lime, it is better to decompose the carbonate with an acid.

Preparation of carbonic acid gas.—The form of the calcium carbonate, and the nature of the acid employed, are by no means matters of indifference. If dilute sulphuric acid be poured upon fragments of marble, the effervescence which occurs at first soon ceases, for the surface of the marble becomes coated with the nearly insoluble calcium sulphate, by which it is protected from the further action of the acid—

$$\underset{\text{Marble.}}{CaCO_3} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Calcium sulphate.}}{CaSO_4} + H_2O + CO_2;$$

if the marble be finely powdered, or if powdered chalk be employed, each particle of the carbonate will be attacked. When lumps of calcium carbonate are acted upon by hydrochloric acid, there is no danger that any will escape the action of the acid, for the calcium chloride produced is one of the most soluble salts—

$$\underset{\text{Marble.}}{CaCO_3} + 2HCl = \underset{\text{Calcium chloride.}}{CaCl_2} + H_2O + CO_2.$$
$$\text{Hydrochloric acid.}$$

For the ordinary purposes of experiment, carbonic acid gas is most easily obtained by the action of hydrochloric acid upon small fragments of marble contained either in a two-necked bottle (Fig. 11) or in the centre bulb of a *Kipp's* apparatus (Fig. 89). The gas should be washed by passing it through a little water in a wash-bottle and may be collected by downward displacement.

When carbon dioxide is required on a large scale it is used in the form of furnace gases, which contain nitrogen from the air and CO_2 from the combustion of the fuel; or of lime-kiln gases, the CO_2 in which is derived from the limestone; or of fermenting tun gases, consisting of nearly pure CO_2 due to the fermentation of sugar.

73. *Properties of carbon dioxide.*—Carbonic acid gas is invisible, like the gases already examined, but is distinguished by a peculiar pungent odour, as is perceived in soda-water. It is more than half as heavy

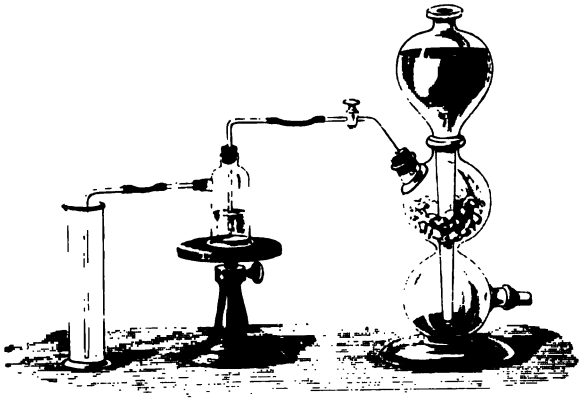


Fig. 89.—Preparation of carbonic acid gas.

again as atmospheric air, its specific gravity being 1.529, which causes its accumulation near the floor of such confined spaces as the Grotto del Cane, where it issues from fissures in the rock.

The high specific gravity of CO_2 may be shown by pouring it into a light jar attached to a balance, and counterpoised by a weight in the opposite scale (Fig. 90).

Fig. 90.

Another favourite illustration consists in floating a soap-bubble on the surface of a layer of the gas generated in the large jar (Fig. 91), by pouring diluted sulphuric acid upon a few ounces of chalk made into a thin cream with water.

If a small balloon, made of collodion, be placed in the jar A (Fig. 92) it will ascend on the admission of carbonic acid gas through the tube B.

If smouldering brown paper be held at the mouth of a jar, like that in Fig. 93, the smoke will float upon the surface of the carbonic acid gas, and will sink with it on removing the stopper.

The power which carbonic acid gas possesses of extinguishing flame is very important, and has received practical application in the case of

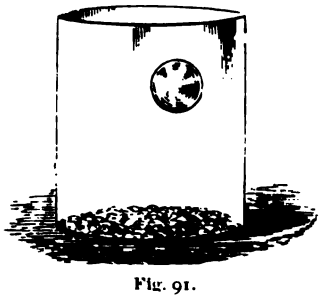


Fig. 91.

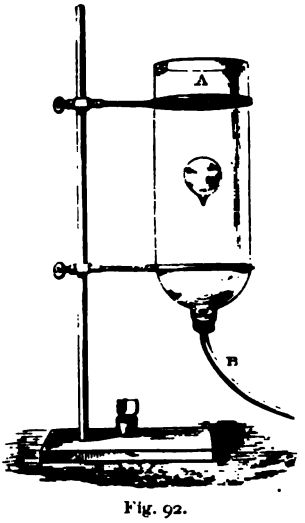


Fig. 92.

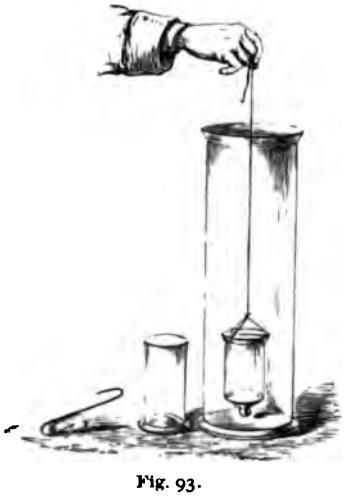


Fig. 93.

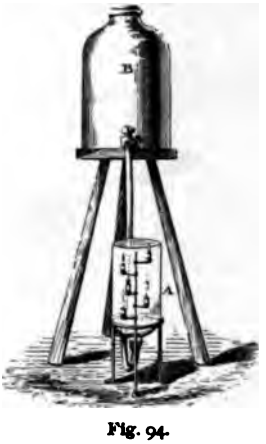


Fig. 94.

burning mines which must otherwise have been flooded with water.* Many attempts have also been made from time to time to employ this gas for subduing ordinary conflagrations, but their success has hitherto been very partial. It will be remembered that pure nitrogen is also capable of extinguishing the flame of a taper, but a large proportion of this gas may be present in air without affecting the flame, whereas a

* All gases which take no part in combustion may extinguish flame, even in the presence of air, by absorbing heat and reducing the temperature below the burning-point.

extinguished in air containing one-eighth of its volume of carcid gas, and is sensibly diminished in brilliancy by a much proportion of the gas.

lle is extinguished in air to which 14 per cent. of its volume of CO_2 has ed: 22 per cent. of nitrogen must be added to produce the same effect. esponding figures for a coal-gas flame are 33 % and 46 %; and for a ı flame 58 % and 70 %.

›wer of extinguishing flame, conjoined with the high density of carbonic admits of some very interesting illustrations.

ı dioxide may be poured from some distance upon a candle, and will ·h it at once. By using a gutter, made of thin wood or stiff paper, to the gas to the flame, it may be extinguished from a distance of several

e torch of blazing tow may be plunged beneath the surface of the carbonic in the jar (Fig. 91).

ı dioxide may be raised in a glass bucket (Fig. 93) from a large jar, ed into another jar, the air in which has been previously tested with a

stand with several tapers fixed at different levels may be placed in the ig. 94), and carbon dioxide gradually admitted through a flexible tube conith the neck of the jar, from the cistern B, a hole in the cover of which r to enter it as the gas flows out; the flame of each taper will gradually the surface of the gas rises in the jar.

of oxygen may be placed over a jar of CO_2, as shown in Fig. 51, and a down through the oxygen, in which it will burn brilliantly, into the CO_2, tinguishes it, and if it be quickly raised again into the oxygen, it will with a slight detonation. This alternate extinction and rekindling may ed several times.

ccount of this extinguishing power of carbonic acid gas, a taper continue to burn in a confined portion of air until it has ted the oxygen, but only until its combustion has produced a ıt quantity of carbon dioxide to extinguish the flame.*

monstrate this, advantage may be taken of the circumstance that phosvill continue to burn in spite of the presence of carbonic acid gas. Upon l A (Fig. 95) a small piece of phosphorus is placed, and a taper attached to d by a wire. The cork B fits air-tight into the jar, and carries a piece of ire bent so that it may be heated by the flame of r. A little water is poured into the plate to preentrance of any fresh air. If the taper be kindled, jar placed over it, the flame will soon die out; noving the jar so that the hot wire may touch the rus, its combustion will show that a considerable of oxygen still remains.

Fig. 95.

ıe same manner, an animal can breathe a d portion of air only until he has charged so much carbonic acid gas that the hurtful f this gas begins to be felt, a considerable quantity of oxygen naining.

air contained in the jar A (Fig. 96), standing over water, be breathed two times through the tube B, a painful sense of oppression will soon be felt quence of the accumulation of carbonic acid gas. The air may thus be with 10 volumes of carbonic acid gas in 100 volumes, the oxygen becomced to about one-half its original quantity. By immersing a deflagrating containing a piece of burning phosphorus, and having a lighted taper it may be shown that, although there is enough carbonic acid gas to

* the taper is extinguished, the air contains in 100 volumes 18¾ volumes of oxygen olumes of carbonic acid gas.

extinguish the taper, the oxygen is not exhausted, for the phosphorus continues to burn rapidly.

Carbonic acid gas is not poisonous when taken into the stomach, but acts most injuriously when breathed, by offering an obstacle to the escape of carbonic acid gas, by diffusion, from the blood of the venous circulation in the lungs, and its consequent exchange for the oxygen necessary to arterial blood. Any hindrance to this interchange must impede respiration, and such hindrance would of course be afforded by carbonic acid gas present in the air inhaled, in proportion to its quantity. There is evidently a distinction between air which has had carbon dioxide added to it and air in which there is a like amount of carbon dioxide produced by respiration. Thus air which has had its content of carbon dioxide raised to 1 per cent. by addition of the gas may be breathed with impunity, but if there be this proportion present as a result of respiration the effect on most persons would be very deleterious.

Fig. 96.

Notwithstanding the many attempts which have been made to trace some other product of respiration which might account for the harmful character of expired air, there is still no satisfactory explanation of the observation that the air of a room becomes progressively more unwholesome as the carbon dioxide in it is increased by respiration. It has often been stated, and the statement has as often been controverted, that a specific poison accompanies the products of respiration. It is more probable that the oppressive character of a close room is due to other exhalations from the body, and is not really an effect of the carbon dioxide of the breath.

It is agreed amongst those who concern themselves with ventilation that the percentage of carbon dioxide in the air of a room or building is an index of the wholesomeness of the air. Thus it is considered inadvisable to breathe for any length of time in air containing more than 10 volumes of CO_2 in 10,000 volumes (0.1 per cent.). The air of a room contains too much CO_2 if half a measured ounce of lime-water becomes turbid when shaken in a half-pint bottle of the air.

When the carbon dioxide amounts to 50 volumes per 10,000 volumes of air (0.5 per cent.) most persons are attacked by the languor and headache attending bad ventilation. A large proportion of carbonic acid gas produces insensibility, and air containing 20 per cent. of its volume causes suffocation. The danger in entering old wells, cellars, and other confined places, is due to the accumulation of this gas, either exhaled from the earth or produced by decay of organic matter. The ordinary test applied to such confined air by introducing a candle is only to be depended upon if the candle burns as brightly in the confined space as in the external air; should the flame become at all dim, it would be unsafe to enter, for experience has shown that combustion may continue for some time in an atmosphere dangerously charged with carbonic acid gas.

The accidents from *choke damp* and *after damp* in coal mines, and from the accumulation, in brewers' and distillers' vats, of the carbonic acid gas resulting from fermentation, are also examples of its fatal effect.

The air issuing from the lungs of a man at each expiration contains from 4 to 4.5 volumes of carbonic acid gas in 100 volumes of air, and could not, therefore, be breathed again without danger. The total amount of carbonic acid gas evolved by the lungs and skin amounts to about 0.7 cubic foot per hour. Adding this to the carbonic acid gas already present in the air (say 0.04 per cent.), the total should be distributed through at least 3500 cubic feet, in order that it may be breathed again with perfect safety, that is, in order that the CO_2, which is regarded as the indicator, should not exceed 0.06 per cent. by volume. Hence the necessity for a constant supply of fresh air by ventilation, to dilute the expired air to such an extent that it may cease to impede respiration. This becomes the more necessary where a demand is made on the atmospheric oxygen by candles or gas-lights. An ordinary gas-burner consumes at least 3 cubic feet of gas per hour, which requires rather more than its own

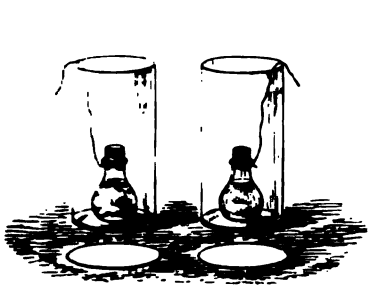


Fig. 97.

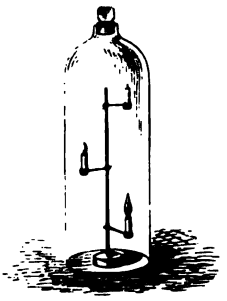


Fig. 98.

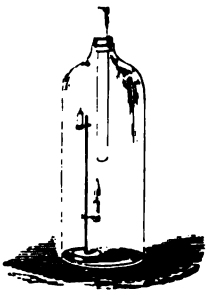


Fig. 99.

volume of oxygen for combustion, and produces about 1.7 cubic foot of carbonic acid gas. Fortunately, a natural provision for ventilation exists in the circumstance that the processes of respiration and combustion, which contaminate the air, also raise its temperature, thus diminishing its specific gravity by expansion, and causing it to ascend and give place to fresh air. Hence the vitiated air always accumulates near the ceiling of an apartment, and it becomes necessary to afford it an outlet by opening the upper sash of the window, since the chimney ventilates immediately only the lower part of the room.

These principles may be illustrated by some very simple experiments.

Two quart jars (Fig. 97) are filled with carbonic acid gas, and after being tested with a taper, a 4-oz. flask is lowered into each, one flask containing cold and the other hot water. After a few minutes the jar with the cold flask will still contain enough carbonic acid gas to extinguish the taper, whilst the air in the other jar will support combustion brilliantly.

A tall stoppered glass jar (Fig. 98) is placed over a stand, upon which three lighted tapers are fixed at different heights. The vitiated air, rising to the top of the jar, will extinguish the uppermost taper first, and the others in succession. By quickly removing the stopper and raising the jar a little before the lowest taper has expired, the jar will be ventilated and the taper revived.

A similar jar (Fig. 99), with a glass chimney fixed into the neck through a cork

or piece of vulcanised tubing, is placed over a stand with two tapers, one of which is near the top of the jar, and the other beneath the aperture of the chimney: if a crevice for the entrance of air be left between the jar and the table, the lower taper will continue to burn indefinitely, whilst the upper one will soon be extinguished by the carbonic acid gas accumulating around it.

In ordinary apartments, the incidental crevices of the doors and windows are depended upon for the entrance of fresh air, whilst the contaminated air passes out by the chimney; but in large buildings special provision must be made for the two air currents. In mines this becomes the more necessary, since the air receives much additional contamination by the gases (marsh-gas and carbon dioxide) evolved from the workings, and by the smoke occasioned in blasting with gunpowder. Mines are generally provided with two shafts for ventilation, under one of which (the *upcast* shaft) a fire is maintained to produce the upward current, which carries off the foul air, whilst the fresh air descends by the other (*downcast* shaft). The current of fresh

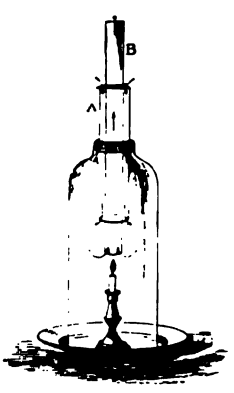


Fig. 100.

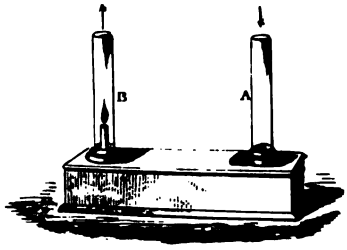


Fig. 101.

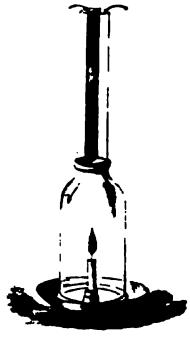


Fig. 102.

air is forced by wooden partitions to divide itself, and to pass through every portion of the workings.

The operation of such provisions for ventilation is easily exhibited.

A tall jar (Fig. 100) is fitted with a ring of cork, carrying a wide glass chimney (A). If this be placed over a taper standing in a plate of water, the accumulation of vitiated air will soon extinguish the taper; but if a second chimney (B), supported in a wire ring, be placed within the wide chimney, fresh air will enter through the interval between the two, and the smoke from a piece of brown paper will demonstrate the existence of the two currents, as shown by the arrows.

A small box (Fig. 101) is provided with a glass chimney at each end. In one of these (B) representing the upcast shaft, a lighted taper is suspended. A piece of smoking brown paper may be held in each chimney to show the direction of the current. On closing A with a glass plate, the taper in B will be extinguished, the entrance of fresh air being prevented. By breathing gently into A the taper will also be extinguished. The experiment may be varied by pouring carbon dioxide and oxygen alternately into A, when the taper will be extinguished and rekindled by turns.

A pint bell-jar (Fig. 102) is placed over a taper standing in a tray of water. If a chimney (a common lamp-glass) be placed on the top of the jar, the flame of the taper will gradually die out, because no provision exists for the establishment of the two currents, but on dropping a piece of tinplate or cardboard into the chimney so

as to divide it, the taper will be revived, and the smoke from the brown paper will distinguish the upcast from the downcast shaft.

If a little water be poured into a wide-mouthed bottle of carbon dioxide, and the bottle be then firmly closed by the palm of the hand, it will be found, on shaking the bottle violently, that the gas is absorbed, and the palm of the hand is sucked into the bottle. The presence of carbonic acid in the solution may be proved by pouring it into lime-water, in which it will produce a precipitate of calcium carbonate, redissolved by a further addition of the solution of carbonic acid.

One pint of water shaken in a vessel containing carbonic acid gas, at the ordinary pressure of the atmosphere, and at the ordinary temperature, will dissolve about one pint of the gas, equal in weight to nearly 16 grains. If the gas be confined in the vessel under a pressure equal to twice or thrice that of the atmosphere—that is, if twice or thrice the quantity of gas be compressed into the same space—the water will still dissolve one pint of the gas, but the weight of this pint will now be twice or thrice that of the pint of uncompressed gas, so that the water will have dissolved 32 or 48 grains of the gas, accordingly as the pressure had been doubled or trebled. As soon, however, as the pressure is removed, the compressed carbonic acid gas will resume its former state, with the exception of that portion which the water is capable of retaining in solution under the ordinary pressure of the atmosphere. Thus, if the water had been charged with carbonic acid gas under a pressure equal to thrice that of the atmosphere, and had therefore absorbed 48 grains of the gas, it would only retain 16 grains when the pressure was taken off, allowing 32 grains to escape in minute bubbles, producing the appearance known as *effervescence*. This affords an explanation of the properties of soda-water, which is prepared by charging water with carbonic acid gas under considerable pressure, and rapidly confining it in strong bottles. As soon as the resistance offered by the cork to the expansion of the gas is removed, the excess above that which the water can hold in solution at the ordinary pressure of the air, escapes with effervescence. In a similar manner the waters of certain springs become charged with carbonic acid gas, under high pressure, beneath the surface of the earth, and when, upon their rising to the surface, this pressure is removed, the excess escapes with effervescence, giving rise to the sparkling appearance and sharp flavour which render spring water so agreeable. On the other hand, the waters of lakes and rivers are usually flat and insipid, because they hold in solution so small a quantity of carbonic acid gas.

The solution of CO_2 in water is believed to contain the true *carbonic acid* or *hydrogen carbonate*, H_2CO_3, or $CO(OH)_2$, for $CO_2 + H_2O = H_2CO_3$, but there is no direct evidence in support of this view.

The sparkling character of champagne, bottled beer, &c., is due to the presence in these liquids of a quantity of carbonic acid gas which has been generated by fermentation subsequent to bottling, and has therefore been retained in the liquid under pressure. In the case of Seidlitz powders and soda-water powders, the effervescence caused by dissolving them in water is due to the disengagement of carbonic acid gas, by the action of the tartaric acid, which composes one of the powders, upon the bicarbonate of soda composing the other powder, producing tartrate

of soda and carbonic acid gas. In the dry state these powders may be mixed without any chemical change, but the addition of water immediately causes the effervescence. Many *baking powders* are mixtures of this kind, being used for imparting lightness and porosity to bread and cakes, by distending the dough with bubbles of carbonic acid gas.

The solubility of carbonic acid in water is of great importance in the chemistry of nature; for this acid, brought down from the atmosphere dissolved in rain, is able to act chemically upon rocks, such as granite, which contain alkalies—the carbonic acid attacking these, and thus slowly disintegrating or crumbling down the rock, an effect much assisted by the mechanical action of the expansion of freezing water in the interstices of the rock. It appears that soils are thus formed by the slow degradation of rocks, and when these soils are capable of supporting plants, the solution of carbonic acid is again of service, not only as possibly providing the plant with carbon through its roots, but as a solvent for certain portions of the mineral food of the plant (such as calcium phosphate), which pure water could not dissolve, and which the plant cannot take up except in the dissolved state.

74. *Liquefaction of carbon dioxide.*—It is generally found that the greater the solubility of a gas in water the more easily the gas can be liquefied; thus CO_2 is much more easily liquefied than is either hydrogen or oxygen. At about the ordinary temperature (63° F., 17° C.), a pressure of 54 atmospheres (800 lbs. per square inch) condenses the gas to a colourless liquid of sp. gr. 0.83 (water = 1), and boiling-point − 80° C. If the temperature of the gas is reduced to 0° C., a pressure of 35 atmospheres suffices to liquefy it.

Liquid carbon dioxide dissolves in alcohol and in ether, but not in water. When allowed to evaporate rapidly so much heat is absorbed by its passage into the gaseous state that a part of the liquid becomes solid carbon dioxide, a snow-like substance, of specific gravity 1.4.

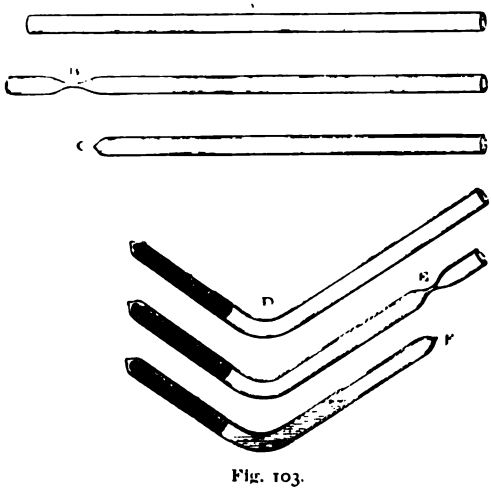


Fig. 103.

The critical temperature (p. 29) of carbon dioxide is 31° C. It is worthy of note that nitrous oxide, which has the same molecular weight as carbon dioxide, has nearly the same critical temperature and boiling-point.

A small specimen of liquid carbon dioxide is easily prepared. A strong glass tube (A. Fig. 103) is selected, about 12 inches long, $\frac{1}{8}$ inch diameter in the bore, and $\frac{1}{16}$ inch thick in the walls. With the aid of the blow-pipe flame this tube is softened and drawn off at about an inch from one end, as at B, which is thus closed (C). This operation should be performed slowly, in order that the closed end may not be much thinner than the walls of the tube. When the tube has cooled,

between 30 and 40 grs. of powdered bicarbonate of ammonia (ordinary sesquicarbonate which has crumbled down) are tightly rammed into it with a glass rod. This part of the tube is then surrounded with a few folds of wet blotting-paper to keep it cool, and the tube is bent, just beyond the carbonate of ammonia to a somewhat obtuse angle (D). The tube is then softened at about an inch from the open end, and drawn out to a narrow neck (E), through which a measured drachm of oil of vitriol is poured down a funnel-tube, so as not to soil the neck, which is then carefully drawn out and sealed by the blowpipe flame, as at F. The empty space in the tube should not exceed ½ cubic inch.

When the tube is thoroughly cold, it is suspended by strings in such a position that the operator, having retired behind a screen at some distance, may reverse the tube, allowing the acid to flow into the limb containing the carbonate of ammonia; or the tube may be fixed in a box which is shut up, and reversed so as to bring the tube into the required position.

If the tube be strong enough to resist the pressure, it will be found, after a few hours, that a layer of liquid CO_2 has been formed upon the surface of the solution of ammonium sulphate. By cooling the empty limb in a mixture of pounded ice and salt, or of hydrochloric acid and sodium sulphate, the liquid can be made to distil itself over into this limb, leaving the ammonium sulphate in the other.

Liquid CO_2 is now sold in steel cylinders provided with screw valves, like those containing compressed oxygen (Fig. 40). When the cylinder is turned on its head and the valve is opened, the liquid is ejected, and at once solidifies to carbonic acid "snow," which may be collected by surrounding the nozzle with sacking. The solid should be quickly shaken on to a sheet of paper, and emptied into a beaker placed within a larger beaker, the interval being filled up by flannel. By covering the beaker with a dial glass, the solid may be kept for some time.

The solid carbon dioxide evaporates without melting, for its own evaporation keeps it at a temperature below its melting-point. It produces a sharp sensation of cold when placed upon the hand, and if pressed into actual contact with the skin causes a painful frost-bite. Its rapid evaporation may be shown by placing a few fragments on the surface of water in the globe (Fig. 104), which has a tube passing down to the bottom, through which the pressure of the carbonic acid gas forces the water to a considerable height.

Fig. 104.

The solid carbon dioxide is soluble in ether, and it evaporates from this solution far more rapidly, because the liquid is a better conductor of heat than the highly porous solid, and abstracts heat more rapidly from surrounding objects.

It thus lowers the temperature to the boiling-point of CO_2.

If a layer of ether be poured upon water, and some solid carbon dioxide be thrown into it, the water is covered with a layer of ice.

On immersing the bulb of a thermometer into the solution of solid carbon dioxide in ether, the mercury becomes solid, and the bulb may be hammered out into a disk.

By placing a piece of filter-paper in an evaporating dish, pouring a pound or so of mercury into it, immersing a wire turned into a flat spiral at the end, covering the mercury with ether, and throwing in some solid carbon dioxide, the mercury may soon be frozen into a cake. If this be suspended by the wire in a vessel of water, the mercury melts, descending in silvery streams to the bottom of the vessel, leaving a cake of ice on the wire, with icicles formed during the descent of the mercury. This experiment is rendered more effective by using an inverted gas-jar, to the neck of which is attached, by a perforated cork, a test-tube to catch the mercury. The round lid of a cardboard box gives a nice disk of frozen mercury.

Even in a red-hot vessel, with prompt manipulation, the mercury may be solidified by the solution of solid carbon dioxide in ether. For this purpose a platinum dish is heated to redness over a large Bunsen burner, a few lumps of carbon dioxide are thrown into it, upon these is held a copper or platinum dish containing the mercury, in which is also held a wire to serve as a handle for withdrawing the mercury. Some more carbon dioxide is thrown upon the mercury, and ether is spirted on to it from a small washing-bottle. One or two additions of the carbon

dioxide and ether alternately will freeze the mercury, which may be withdrawn from the flames by the wire handle.

Carbon dioxide is advantageously used in freezing-machines on the principle described for ammonia (p. 82); for although it absorbs much less heat in passing from the liquid to the gaseous state (about 60 cals. per gram. at 10° C. as against 320 cals. for ammonia), the volume to be pumped per unit weight is much less.

75. Carbonic acid gas may be separated from most other gases by the action of potash, which absorbs it, forming potassium carbonate. The proportion of carbonic acid gas is inferred, either from the diminution in volume suffered by the gas when treated with potash, or from the increase of weight of the latter.

In the former case the gas is carefully measured over mercury (Fig. 105), with due attention to temperature and barometric pressure, and a little concentrated solution of potash is thrown up through a curved *pipette* or syringe, introduced into the orifice of the tube beneath the surface of the mercury. The tube is gently shaken for a few seconds to promote the absorption of the gas, and, after a few minutes' rest, the diminution of volume is read off. Instead of solution of potash, damp potassium hydroxide in the solid state is sometimes introduced, in the form of small sticks or balls attached to a wire. To determine the weight of carbonic acid gas in a gaseous mixture, the latter is passed through a bulb-apparatus (H, Fig. 81), containing a strong solution of potash, and weighed before and after the passage of the gas. A little tube, containing solid potash, or calcium chloride, or pumice-stone moistened with sulphuric acid, must be attached to the bulb-apparatus, for the purpose of retaining any vapour of water which the large volume of unabsorbed gas might carry away in passing through the solution of potash.

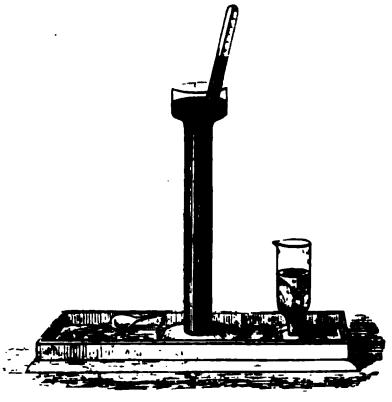


Fig. 105.

The method for proving the composition of carbon dioxide by weight has been given at p. 109. Its composition by volume is dealt with on p. 136.

76. *Salts formed by carbonic acid.*—Although so ready to combine with the alkalies and alkaline earths (as shown in its absorption by solution of potash and by lime-water), carbonic acid must be classed among the weaker acids. It does not neutralise the alkalies completely, and it may be displaced from its salts by most other acids. Its action upon the colouring matter of litmus is feeble and transient. If a solution of carbonic acid be added to blue infusion of litmus, a wine-red liquid is produced, which becomes blue again when boiled, losing its carbonic acid; whilst litmus reddened by sulphuric, hydrochloric, or nitric acid, acquires a brighter red colour, which is permanent on boiling. On forcing CO_2 into solution of litmus at several atmospheres pressure a bright red colour is produced; but this is not permanent.

With each of the alkalies carbonic acid forms two well-defined salts, the *carbonate* and *bicarbonate*. Thus, the carbonates of potassium and sodium are represented by the formulæ, K_2CO_3 and Na_2CO_3, whilst the bicarbonates are $KHCO_3$ and $NaHCO_3$. The existence of the latter

salts would favour the belief in the existence of the compound H_2CO_3, although this has not yet been obtained in the separate state.

The formula H_2CO_3 represents carbonic acid as a *dibasic* acid, that is, an acid containing two atoms of H for which metals may be substituted.

Carbonates may be *normal*, *acid*, or *basic*. A normal carbonate is one in which all the hydrogen in H_2CO_3 is exchanged for a metal or metals, as in sodium carbonate, Na_2CO_3, and calcium carbonate, $CaCO_3$.

An acid carbonate is one in which only half of the hydrogen is exchanged for a metal, as in hydrosodium carbonate, $NaHCO_3$. A basic carbonate is a normal carbonate in combination with a hydrate of the metal, as in *white lead*, basic lead carbonate, $2PbCO_3.Pb(OH)_2$.

Perfectly dry carbonic acid gas is not absorbed by pure quicklime (CaO), until it is heated to 350°–400° C.

Two hard glass tubes closed at one end, and bent as in Fig. 106, are perfectly dried, and filled, over mercury, with well-dried carbonic acid gas. Fragments of lime are taken, whilst red hot, out of a crucible, cooled under the mercury, inserted

Fig. 106.

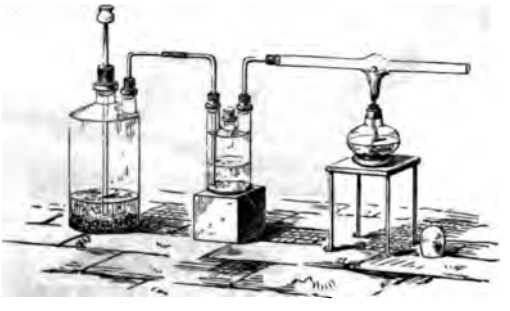


Fig. 107.

into the tubes, and transferred to the upper end. No absorption of the gas occurs, though the tubes be left for some days; but if one of them be heated by a Bunsen burner, the CO_2 is rapidly absorbed, and the mercury is forced up into the tube.

77. To demonstrate the presence of carbon in carbon dioxide, a pellet of potassium is introduced into a bulb tube, through which a current of the gas (dried by passing through oil of vitriol, or over chloride of calcium) is flowing, and the heat of a spirit-lamp is applied to the bulb. The metal soon burns in the gas, which it robs of its oxygen, leaving the carbon as a black mass in the bulb (Fig. 107). The potassium remains in the form of potassium carbonate, $3CO_2 + K_4 = 2K_2CO_3 + C$. If slices of sodium be arranged in a test-tube in alternate layers with dried chalk (calcium carbonate), and strongly heated with a spirit-lamp, vivid combustion will ensue, and much carbon will be separated ($CaCO_3 + Na_4 = CaO + 2Na_2O + C$).

When CO_2 is submitted to the action of electric sparks in an apparatus such as that shown in Fig. 72, it expands slightly, having been partially converted into $CO + O$, but if the sparking is continued, the mixture explodes to form CO_2, restoring the original volume of the gas. In a partial vacuum in which the pressure the CO_2 is only 5 millimetres nearly 70 per cent. of the CO_2 may be decomposed in this way.

Carbon Monoxide or Carbonic Oxide.

CO = 28 parts by weight = 2 volumes.

78. The combustion of potassium or sodium in carbon dioxide deprives the gas of all its oxygen, but other metals, which are not

endowed with so powerful an attraction for oxygen, do not carry the decomposition of carbon dioxide to its final limit; thus, iron, zinc and magnesium at a high temperature only deprive the gas of one-half of its oxygen, a result which may also be brought about at a red heat by carbon itself. If an iron tube filled with fragments of charcoal be heated to redness in a furnace (Fig. 11), and carbon dioxide be transmitted through it, it will be found, on collecting the gas which issues from the other extremity of the tube, that on the approach of a taper the gas takes fire, and burns with a beautiful blue lambent flame, similar to that which is often observed to play over the surface of a clear fire. Both flames, in fact, are due to the same gas, and in both cases this gas is produced by the same chemical change, for, in the tube, the carbon dioxide yields half of its oxygen to the charcoal, both becoming converted into carbonic oxide; $CO_2 + C = 2CO$. In the fire, the carbon dioxide is formed by the combustion of the carbon of the fuel in the oxygen of the air entering at the bottom of the grate; and this CO_2, in passing over the layer of heated carbon in the upper part of the fire, is partly converted into carbonic oxide, which inflames when it meets

Fig. 108.—Reverberatory furnace for copper-smelting.

with the oxygen in the air above the surface of the fuel, and burns with its characteristic blue flame, reproducing carbon dioxide.* The carbon monoxide occupies twice the volume of the carbon dioxide from which it was produced.

This conversion of carbon dioxide into carbon monoxide is of great importance, on account of its extensive application in metallurgic operations. It is often desirable, for instance, that a flame should be made to play over the surface of an ore placed on the bed or hearth of a reverberatory furnace (Fig. 108). This object is easily attained when the coal affords a large quantity of inflammable gas: but with anthracite coal, which burns with very little flame, and is frequently employed in such furnaces, it is necessary to pile a high column of coal upon the grate, so that the carbon dioxide formed beneath may be converted into carbonic oxide in passing over the heated coal above, and when this gas reaches the hearth of the furnace, into which air is admitted, it burns

* It is stated that when the temperature of a fuel in a furnace has attained 1000° C., the carbon burns directly to carbon monoxide. When carbon is heated in partially dried oxygen, carbon monoxide alone is produced, showing that this is the first product of the combustion; it remains carbon monoxide because the oxygen is too dry to burn it to the dioxide (p. 133). The carbon of gaseous carbon compounds burns first to carbon monoxide, which is further oxidised to the dioxide.

with a flame which spreads over the surface of the ore. It is frequently advantageous to make carbon monoxide in this way in a grate (*producer*) at some distance from the furnace and to conduct it thither through pipes. (See *Chemistry of Fuel.*) The temperature of the flame of carbonic oxide burning in air is estimated at about 1400° C.

The attraction of carbonic oxide for oxygen is turned to account in removing that element from combination with iron in its ores, as will be seen hereafter.

Dry carbon monoxide will not combine with dry oxygen unless the mixture of gases be very strongly heated. This fact is an instance of the influence which water vapour exercises in chemical combination (compare p. 32).

It follows that dry carbon monoxide will not burn in dry air or dry oxygen. To demonstrate this fact, carbon monoxide is passed through strong sulphuric acid and kindled at a jet; the flame is introduced into an inverted gas jar containing ordinary air to show that the combustion will continue in such a vessel; the air in a similar jar is now dried by shaking strong sulphuric acid in it, the acid is quickly poured out, and the flame introduced into the inverted jar, whereupon combustion immediately ceases.

Judging by analogy with other elements, whose combination with two atoms of oxygen produces twice as much heat as their combination with one atom, the conversion of C into CO_2 should produce twice as much heat as its conversion into CO. When C, in the form of charcoal, burns to form CO_2, each gram of C produces 8080 gram units of heat: or C, 12 grams, + O_2, 32 grams, = CO_2 + 96,960 units of heat. Now carbon cannot be burned directly to form CO, but when CO burns to form CO_2, 1 gram of CO produces 2403 units of heat; or CO, 28 grams, + O, 16 grams, = CO_2 + 67,284 units of heat. In the first equation, 16 grams of O produce 48,480 units, and in the second 67,284 units of heat. But in the first case, solid carbon is converted into gas, a change of state which must absorb much of the heat produced. If the C were in the state of gas to begin with, in both cases, it is probable that we should have O, 16 grams, + C, 12 grams, = CO + 67,284 units of heat, and O_2, 32 grams, + C, 12 grams, = CO_2 + 134,568 units of heat, so that 1 gram of C would give 11,214 units of heat when burned to CO_2. But when 1 gram of solid C burns to CO_2 it gives only 8080 units of heat: hence 11,214 − 8080, or 3134 units, represent the heat required to convert 1 gram of solid carbon into gas.

79. Carbonic oxide is very poisonous; and it appears that the accidents which too frequently occur from burning charcoal or coke in braziers and chafing-dishes in close rooms, result from the poisonous effects of the small quantity of carbonic oxide which is produced and escapes combustion, since the amount of carbonic acid gas thus diffused through the air is not sufficient, in most cases, to account for the fatal result. The carbonic oxide formed in cast-iron stoves diffuses through the hot metal into the air of a room. It is certainly fatal to breathe air containing 1 per cent. of CO, and it is said that so little as 0.05 per cent. may prove fatal.

80. The poisonous character of carbon monoxide is raised as an objection to the proposed use of this gas for purposes of illumination. The character of the flame of carbonic oxide would appear to afford little promise of its utility as an illuminating agent; but that it is possible so to employ it is easily demonstrated by kindling a jet of the gas which has been passed through a wide tube containing a little cotton moistened with rectified coal naphtha (benzene), when the carbon monoxide will be found to burn with a very luminous flame. The carbonic oxide destined to be employed for illuminating purposes is prepared by passing steam over white hot coke, a mixture of carbon

monoxide and hydrogen being thus produced; $C + H_2O = CO + H_2$. The *water-gas* always contains some carbon dioxide, the quantity being greater the lower the temperature of the coke. This is because at lower temperatures the coke burns in steam to carbon dioxide, not to carbon monoxide; $C + 2H_2O = CO_2 + 2H_2$. Water-gas usually consists of about 50 per cent. of H, 40 per cent. of CO, 5 per cent. of CO_2, and 5 per cent. of N (from air and the coke). Since neither hydrogen nor carbon monoxide is possessed of any odour, this mixture would not be detected in the atmosphere of a room where there was a leaky gas-pipe, and the presence of the poisonous carbon monoxide would remain unsuspected. Thus, it becomes incumbent upon those supplying such gas to dwelling-houses to render it, by mixing some gas or vapour with it, at least as odorous as is ordinary coal-gas, an escape of which is so easily detected.

The application of water-gas in this country, for illuminating purposes, is at present limited to its admixture with coal-gas, for which purpose it is rendered luminous by hydrocarbons obtained from the destructive distillation of petroleum.

The decomposition of steam by red-hot carbon is also taken advantage of in order to procure a flame from anthracite coal when employed for heating boilers. The coal being burnt on *fish-bellied* bars, beneath which a quantity of water is placed, the radiated heat converts the water into steam, which is carried by the draught into the fire, where it furnishes carbonic oxide and hydrogen, both capable of burning with flame under the bottom of the boiler. The temperature of the bars is also thus reduced, so that they are not so much injured by the intense heat of the glowing fuel.

81. Carbonic oxide, unlike carbon dioxide, is nearly insoluble in water. It is even lighter than air, its specific gravity being 0.967. In its chemical relations it is an indifferent oxide, that is, it has neither acid nor basic properties. It is liquid below $-190°$ C. (its boiling-point), and solid at $-211°$ C. (its melting-point). Its critical temperature is $-140°$ C. These constants approximate to the corresponding constants for nitrogen.

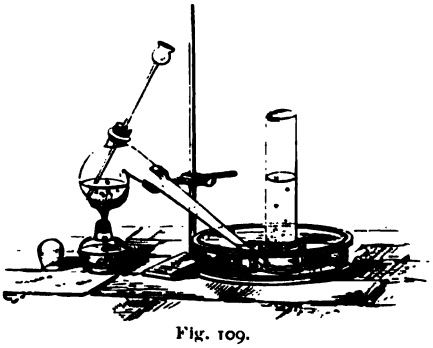


Fig. 109.

82. A very instructive process for obtaining carbonic oxide, consists in heating crystallised oxalic acid with three times its weight of oil of vitriol. If the gas be collected over water (Fig. 109), and one of the jars be shaken with a little lime-water, the milkiness imparted to the latter will indicate abundance of carbon dioxide; whilst, on removing the glass plate, and applying a light, the carbonic oxide will burn with its characteristic blue flame. The gas thus obtained is a mixture of equal volumes of carbonic oxide and carbonic acid gases. Crystallised oxalic acid is represented by the formula $C_2H_2O_4.2Aq$, and if the water of crystallisation be left out of consideration, its decomposition may be represented by the equation $C_2H_2O_4 = H_2O + CO + CO_2$, the change being determined by the attraction of the oil of vitriol for water. To obtain pure CO, the mixture of gases must be passed through a bottle containg solution of potash, to absorb the CO_2 (Fig. 110).

But pure CO is much more easily obtained by the action of sulphuric acid upon crystallised potassium ferrocyanide (yellow prussiate of potash) at a moderate heat. Since the gas contains small quantities of sulphurous and carbonic acid gases, it

must be passed through solution of potash if it be required perfectly pure. The chemical change which occurs in this process is expressed thus :

$$\underset{\text{Potassium ferrocyanide.}}{K_4C_6N_6Fe} + 6H_2O + 6H_2SO_4 = 6CO + \underset{\text{Potassium sulphate.}}{2K_2SO_4} + \underset{\text{Ammonium sulphate.}}{3(NH_4)_2SO_4} + \underset{\text{Ferrous sulphate.}}{FeSO_4}$$

Ten grams of crystallised ferrocyanide, with 135 grams (73 c.c.) of sulphuric acid (sp. gr. 1.84) and 13 grams of water, give about $3\frac{1}{2}$ litres of CO.

If the boiling is continued after the evolution of CO has ceased, much sulphurous acid gas is disengaged ($2FeSO_4 + 2H_2SO_4 = Fe_2(SO_4)_3 + 2H_2O + SO_2$).

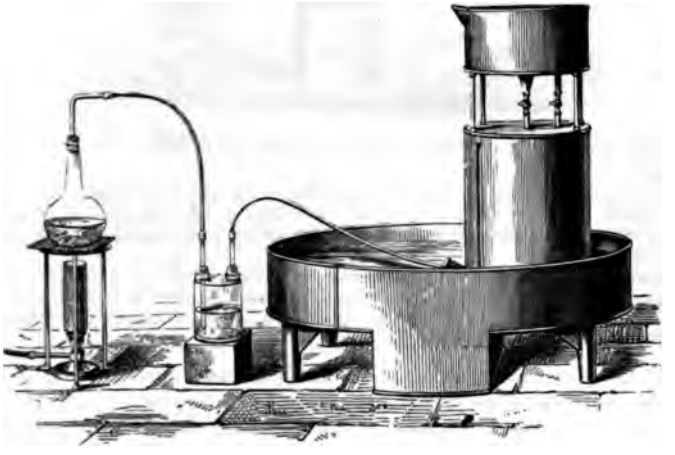


Fig. 110.—Preparation of carbonic oxide.

83. To demonstrate the production of CO_2 during the combustion of CO, a jar of the gas is closed with a glass plate, and after placing it upon the table, the plate is slipped aside and a little lime-water quickly poured into the jar. On shaking, no milkiness indicative of carbonic acid gas should be perceived. The plate is then removed and the gas kindled. On replacing the plate and shaking the jar, an abundant precipitation of calcium carbonate will occur.

Carbonic oxide forms an explosive mixture with half its volume of oxygen ; if the mixture be absolutely free from vapour of water, it does not explode on passing an electric spark through it.

When carbonic oxide is passed through a red-hot porcelain tube, a portion of it is decomposed into carbonic acid gas and carbon ; and when the experiment is conducted without special arrangements, the carbonic oxide is reproduced as the temperature of the gas falls.* But by passing through the centre of the porcelain tube a brass tube, through which cold water is kept running, the decomposition has been demonstrated by the deposition of carbon upon the cooled tube, and by collecting the carbonic acid gas formed. Carbonic acid gas is also decomposed by intense heat into carbonic oxide and oxygen ; but if these gases be allowed to cool down slowly in contact, they recombine. The gas drawn from the hottest region of a blast-furnace (see *Iron*), and rapidly cooled, so as to prevent recombination, was found to contain both carbonic oxide and oxygen.

When electric sparks are passed through carbon dioxide, about one-third of it becomes $CO + O$, but this reaction does not go any further because the $CO + O$ begin to recombine. By passing a pellet of phosphorus into the gas and continuing the sparks, all the CO_2 may be decomposed into $CO + O$, for the phosphorus will combine with the oxygen, and CO_2 cannot be reformed.

The reducing action of carbonic oxide upon metallic oxides, at high temperatures, may be illustrated by passing the pure gas from a bag or gas-holder, first through a bottle of lime-water (B, Fig. 111), to prove the absence of carbonic acid gas, then

* It is stated that CO heated at 500° C. always contains a little CO_2, but no carbon is deposited. If this be true a lower oxide of carbon must be supposed to be formed.

over oxide of copper, contained in the tube C, and afterwards again through lime-water in D. When enough gas has been passed to expel the air, heat may be applied to the tube by the gauze-burner E, when the formation of carbonic acid gas will be immediately shown by the second portion of lime-water, and the black oxide of copper will be reduced to red metallic copper.

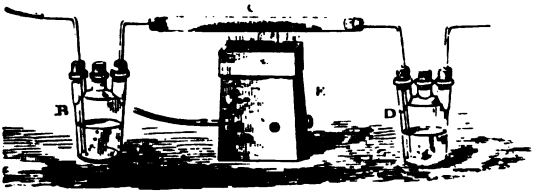


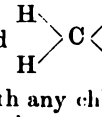
Fig. 111 —Reduction of oxide of copper by carbonic oxide.

If precipitated peroxide of iron be substituted for oxide of copper, iron in the state of black powder will be left, and if allowed to cool in the stream of gas, will take fire when it is shaken out into the air, becoming reconverted into the peroxide (*iron pyrophorus*).

Carbonic oxide is absorbed by potassium hydrate at 100° C., potassium *formate* being produced; $CO + KOH = HCOOK$. If carbonic oxide be passed over soda-lime in a glass tube heated by a gas furnace, sodium carbonate is formed, and hydrogen liberated; $CO + 2NaOH = Na_2CO_3 + H_2$.

84. *Composition by volume of carbon monoxide and carbon dioxide.*— When carbon burns in oxygen, the volume of the carbon dioxide produced is exactly equal to that of the oxygen, so that one volume of oxygen furnishes one volume of carbon dioxide, or, since equal volumes of gases contain the same number of molecules (p. 47), a molecule of carbon dioxide contains a molecule of oxygen.

When one volume of carbon dioxide (containing one volume of oxygen) is passed over heated carbon, it yields two volumes of carbonic oxide; hence two volumes, or one molecule, of this gas contain one volume, or half a molecule, of oxygen.

85. It will be seen in the next few pages that carbon can combine with hydrogen and with chlorine in the sense that one atom of carbon can fix four atoms of hydrogen or of chlorine, but no more. Carbon is therefore the type of the tetravalent elements (p. 11), and may be considered as exerting its affinity in four directions, $>C<$. When all of these affinities are satisfied by the affinities of other elements, the carbon will be unable to combine with any other element. Thus, the carbon in the compound  will be unable to combine with any more hydrogen or with any chlorine; this compound, CH_4, is therefore said to be a *saturated compound*. It has already been seen that oxygen exerts affinity in two directions, $-O-$; consequently one atom of oxygen is equivalent to two atoms of hydrogen in saturating power, and carbon dioxide is a saturated compound, $O< >C< >O$. On the other hand, carbon monoxide should be an *unsaturated compound*, $>C< >O$, and should be capable of combining with other elements in a manner not possible for carbon dioxide. Thus it will be found in the sequel that carbon monoxide is much more chemically active than the

dioxide; it will combine directly with chlorine to form the compound $Cl_2C{<}{>}O$, and with many of the metals. The fact that carbon monoxide combines with oxygen with liberation of heat is in itself an indication of the *residual affinity* of the carbon in carbon monoxide.

Compounds of Carbon with Hydrogen.

86. No two other elements are capable of occurring in so many different forms of combination as are carbon and hydrogen. The *hydrocarbons*, as these compounds are generally designated, include most of the inflammable gases which are commonly met with, and a great number of the essential oils, naphthas, and other useful substances. There is reason to believe that all these bodies, even such as are found in the mineral kingdom, have been originally derived from vegetable sources, and their history belongs, therefore, to the department of organic chemistry. The three simplest examples of such compounds will, however, be brought forward in this place to afford a general insight into the mutual relations of these two important elements.

87. **Acetylene** ($C_2H_2 = 26$ parts by weight).—When very intensely heated, carbon can combine with hydrogen to form acetylene. The necessary temperature is produced by the *electric arc*, that is, the electrical discharge between two pieces of dense carbon (electrodes) connected with the opposite terminals of a source of electric current, such as a dynamo or a powerful galvanic battery. When this arc is surrounded by an atmosphere of hydrogen some acetylene is formed. The experiment has no practical importance, because but little acetylene is obtained in proportion to the energy employed, but its theoretical interest is very great, since it is the first step in the production of organic substances by the direct synthesis of mineral elements; acetylene (C_2H_2) being convertible into olefiant gas (C_2H_4), this last into alcohol (C_2H_6O) and alcohol into a very large number of organic products.

The electric arc is, however, used indirectly for the production of acetylene. For this purpose a mixture of lime and carbon, in the form of coke or charcoal, is heated by the arc in order to make *calcium carbide*, CaC_2, an evil smelling, grey, crystalline substance which yields acetylene and slaked lime when treated with water, $CaC_2 + 2H_2O = C_2H_2 + Ca(OH)_2$.

In places remote from gas-works, acetylene, made from calcium carbide and water, is burnt as an illuminant instead of coal gas, which it exceeds in illuminating value nearly 15-fold. Thus the manufacture of calcium carbide has become an industry and will receive attention in the section devoted to calcium compounds, but a word may be said here about the *electric furnace* to the development of which in recent years we owe several useful substances beside calcium carbide.

This furnace is varied in form to suit the particular requirement, but consists in principle of an electric arc, radiation from which is prevented by a fire-brick casing. The material to be heated is introduced, as far as possible, between the electrodes where the temperature may rise as high as 3500° C. This is a much higher temperature than

that attainable (about 1500° C.) in any furnace heated with ordinary fuel, and chemical changes occur in the electric furnace which cannot be otherwise produced. Such a furnace is shown in perspective in Fig. 112. The shell of the furnace *A* is here cut away to show the position of the carbon electrodes *B*, which are mounted in metal clamp

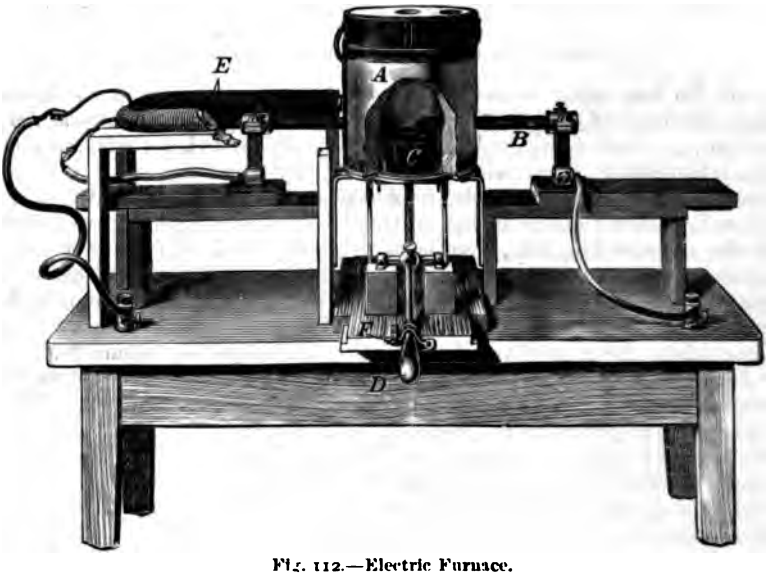


Fig. 112.—Electric Furnace.

carried on slides and connected by leads with the current supply terminals. In series with the electrodes is an electromagnet *E*, by means of which the arc may be deflected in any required direction, for example, down into the crucible *C* containing the body to be heated. The crucible is carried on a suitable platform which is raised or lowered by a lever, the handle *D* of the lever being held by a catch *F*, when the platform which also forms the bottom of the furnace, is in position. When lowered, platform and crucible can be withdrawn from below the furnace by means of the slide shown in the figure. Fig. 113 shows another form of mounting for the carbon electrode, adapted for inserting the carbon through a hole in the lid of the furnace and turning, raising, or lowering it, so as to make any required angle with the other carbon or the crucible.

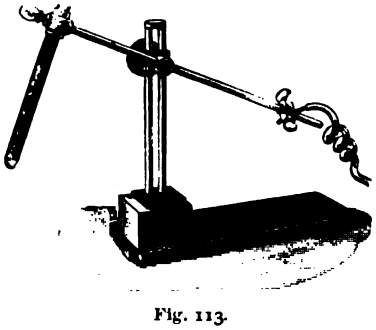


Fig. 113.

Unless calcium carbide is preserved in hermetically sealed vessels it is speedily decomposed by the moisture of the air, and it is to the impure acetylene evolved by this action that the carbide owes its evil odour.

This chemical change evolves a considerable amount of heat (28,500 gram-units of heat per 64 grams of CaC_2), a fact which must not be neglected in making acetylene from the carbide; for the gas is not only explosive when mixed with air or oxygen, as is hydrogen, but explodes by itself when suddenly heated under a pressure of two atmospheres, a pressure which may easily obtain in a carelessly constructed generator. This explosion of the unmixed gas is due to the separation of its elements, $C_2H_2 = C_2 + H_2$.

To prepare acetylene in the laboratory 10 grams of calcium carbide are introduced into a flask which is then fitted with a dropping funnel and a delivery tube (Fig. 114). Water * is allowed to drop slowly from the funnel on to the carbide and the gas is collected over water, care being taken that all air is first expelled from the flask by the issuing gas (see above). It will be noted that the carbide becomes hot and swells, behaving like quicklime when it is slaked to calcium hydroxide, which indeed is the residue left in the flask when all the gas has been evolved.

On a large scale it is not considered safe to drop water on to the carbide, because the temperature is liable to rise unduly. Instead, the carbide is dropped into water so that there may always be an excess of the latter to absorb the heat and keep the generator cool. Moreover, the excess of water dissolves some of the impurities, ammonia and sulphuretted hydrogen, from the gas.

The amount of acetylene obtainable from a given weight of pure calcium carbide has been ascertained by careful analysis, and the result is expressed by the equation $CaC_2 + 2H_2O = C_2H_2 + Ca(OH)_2$, that is to say, $40 + 12 \times 2 = 64$ parts by weight of CaC_2 yield $12 \times 2 + 1 \times 2 = 26$ parts by weight of C_2H_2. If the parts by weight be grams the acetylene will measure 22.22 litres at 0° C. and 760 mm. (see p. 47). Thus the 10 grams of the carbide used above would yield about 3.5 litres of acetylene. But the commercial carbide is far from pure, and seldom yields more than 80 per cent. of the theoretical volume of acetylene. The impurities in the carbide also evolve gases, the chief of which are the evil smelling phosphoretted hydrogen and sulphuretted hydrogen. To rid the acetylene of the latter it must be passed through a wash-bottle containing caustic soda, and the former is then removed by a second bottle containing nitric acid and cupric nitrate.

Acetylene is constantly found among the products of the incomplete combustion and destructive distillation of substances rich in carbon; hence it is always present in small quantity in coal gas, and may be produced in abundance by passing the vapour of ether through a red-hot tube. The character by which acetylene is most easily recognised is that of producing a fine red precipitate (*cuprous acetylide*) in an ammoniacal solution of cuprous chloride.

The original process for preparing this precipitate, is that in which the acetylene is produced by the imperfect combustion occurring when a jet of atmospheric air is allowed to burn in coal gas.

An *adapter* (A, Fig. 114) is connected at its narrow end with a pipe supplying coal gas. The wider opening is closed by a bung with two holes, one of which receives a piece of brass tube (B) about three-quarters of an inch wide and 7 inches long, while in the other is inserted a glass tube (C) which conducts the gas to the bottom of a *separating funnel* (D). The lower opening of the brass tube B is closed with a cork, through which passes the glass tube E connected with a gas-holder or bag containing atmospheric air. To commence the operation, the gas is turned on through the tube F, and when all air is supposed to be expelled, the tube E is withdrawn, together with its cork, and a light is applied to the lower opening of the brass tube, the supply of coal gas being so regulated that it shall burn with a small flame at the end of the tube. A feeble current of air is then

* A saturated solution of salt has been recommended as preferable to pure water; it has a less energetic action on the carbide, so that the temperature does not rise so high.

allowed to issue from the tube E, which is passed up through the flame into the adapter, where the jet of air continues to burn in the coal gas,* and may be kept burning for hours with a little attention to the proportions in which the gas and air are supplied. A solution of cuprous chloride in ammonia is poured into the separating funnel through the lateral opening G, so that the imperfectly burnt gas may pass through it, when the cuprous acetylide is precipitated in abundance. When a sufficient quantity of precipitate has been formed, or the copper solution is exhausted, the liquid is run out through the stopcock (H) on to a filter, and a fresh portion introduced. By heating the precipitate with HCl acetylene is evolved.

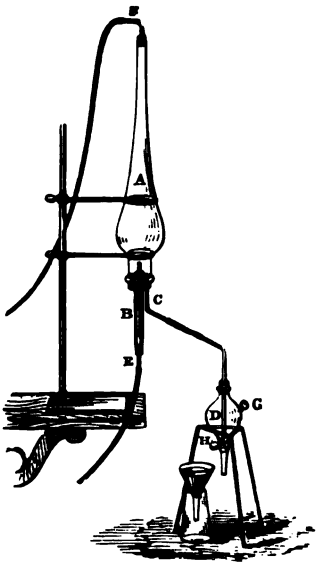


Fig. 114.
Preparation of cuprous acetylide.

A solution of cuprous chloride suitable for this experiment is conveniently prepared in the following manner: 500 grains of black oxide of copper are dissolved in 7 measured ounces of common hydrochloric acid, in a flask, and boiled for about twenty minutes with 400 grains of copper in filings or fine turnings. The brown solution of cuprous chloride in hydrochloric acid, thus obtained, is poured into about 3 pints of water contained in a bottle; the white precipitate (cuprous chloride) is allowed to subside, the water drawn off with a siphon, and the precipitate rinsed into a 20-ounce bottle, which is then quite filled with water and closed with a stopper. When the precipitate has again subsided, the water is drawn off, and 4 ounces of powdered chloride of ammonium are introduced, the bottle being again filled up with water, closed and shaken. The cuprous chloride is entirely dissolved by the chloride of ammonium, but would be precipitated if more water were added. When required for the precipitation of acetylene, the solution may be mixed with about one-tenth of its bulk of strong ammonia (0.880), which may be poured into the separating funnel (D) before the copper solution is introduced. Four measured ounces of the solution are sufficient for one charge, and yield, in three hours, about 3 measured ounces of the moist precipitate. The blue solution of ammoniacal cupric chloride, filtered from the red precipitate, may be rendered serviceable again by being shaken, in a stoppered bottle, with precipitated copper, prepared by reducing a solution of sulphate of copper, acidified with hydrochloric acid, with a plate of zinc.

If the acetylene copper precipitate be collected on a filter, washed, and dried, either by mere exposure to the air, or over oil of vitriol, it will be found to explode with some violence when gently heated, and it is said that the accidental formation of this compound in copper or brass pipes, through which coal gas passes, has occasionally given rise to explosions.

When acetylene purified from phosphoretted and sulphuretted hydrogen is passed through solution of nitrate of silver, a white curdy precipitate is formed, resembling chloride of silver in appearance, but insoluble in ammonia (which turns it yellow) as well as in nitric acid.

It may be more easily prepared by suspending a funnel over a Bunsen burner which has caught fire inside the tube, and drawing the products of imperfect combustion, by means of an aspirator, through a solution of silver nitrate. This precipitate may also be used for the preparation of acetylene, by heating it with hydrochloric acid.

* It is advisable to attach a piece of thin platinum wire to the mouth of the glass tube to render the flame of the air more visible.

When this precipitate is washed and allowed to dry, it is violently explosive if heated or struck, particularly when it has been prepared from a slightly ammoniacal solution of nitrate of silver. A minute fragment of it placed on a glass plate, and touched with a red-hot wire, detonates loudly and shatters the glass like fulminate of silver. In a solution of hyposulphite of gold and sodium, acetylene gives a yellowish, very explosive precipitate.

The copious formation of acetylene during the imperfect combustion of ether, is very readily shown by introducing a few drops of ether into a test-tube, adding a little ammoniacal solution of cuprous chloride, kindling the ether vapour at the mouth of the tube, and inclining the latter so as to expose a large surface of the copper solution, when a large quantity of the red cuprous acetylide is produced. If nitrate of silver be substituted for the copper solution, the white precipitate of silver acetylide is formed abundantly.

Acetylene is a colourless gas having a peculiar odour, which is always perceived where coal gas is undergoing imperfect combustion. It burns with an extraordinarily bright smoky flame, best seen by dropping a piece of calcium carbide into a test-tube containing some water and inserting a cork carrying a jet at which the gas may be ignited when all the air has been expelled. Its most remarkable property is that of inflaming spontaneously when brought in contact with chlorine. If a jet of the gas be allowed to pass into a bottle of chlorine, it will take fire and burn with a red flame, depositing much carbon. When chlorine is decanted up into a cylinder containing acetylene standing over water, a violent explosion immediately takes place, attended with a vivid flash, and separation of a large amount of carbon; $C_2H_2 + Cl_2 = C_2 + 2HCl$.*

Water absorbs about its own volume of the gas. The solution smells strongly of the gas, and yields a decided precipitate with ammoniacal cuprous chloride and with silver nitrate. Alcohol is a better solvent for acetylene, while acetone dissolves about 25 times its volume at 15° C. Acetylene is liquid at 0° C. under 38 atmospheres pressure and at −85° C., at 760 mm.; hence the latter temperature is its boiling-point. The critical temperature is 37° C., and the critical pressure 67 atmospheres. Liquid acetylene is colourless and its sp. gr. is 0.45 at 0° C.

If the acetylene copper precipitate be suspended in solution of ammonia, and heated with a little granulated zinc, the acetylene combines with the (*nascent*) hydrogen to form olefiant gas (C_2H_4). Further particulars respecting acetylene are given under *Organic Chemistry*.

The heat evolved by the combustion of a given weight of acetylene is more than that produced when the same weight of a mixture containing the same proportion of carbon and hydrogen, such as would be obtained by suspending carbon dust in hydrogen, is burnt. This shows that acetylene is an endothermic compound (p. 96).

When 26 grams of C_2H_2, containing 24 grams of C and 2 grams of H, are burnt, 315,000 gram units of heat are evolved; but when these weights of C and H are burnt separately, or merely mixed together, only 257,000 units are evolved. The difference, + 58,000 units, must be due to the disruption of the combination between the C and H in the acetylene; that is, the *heat of formation* of acetylene must be − 58,000.

When 16 grams of methane, CH_4, containing 12 grams of C and 4 grams of H, are burnt, 213,000 gram units of heat are evolved. The same weights of C and H, burnt in mixture give 231,000 units. In this case, therefore, 18,000 units of heat must have been *absorbed* in disuniting the C and H in the methane, so that this compound is exothermic, its heat of formation being + 18,000.

* It is said that a trace of air is essential for the explosion.

Endothermic compounds are liable to decompose suddenly, or detonate, when subjected to a shock. Thus when a small quantity (0.1 gram) of the explosive compound mercuric fulminate is fired in acetylene, the gas explodes, although no oxygen is present other than the small quantity in the fulminate. A similar result follows if a wire heated to about 750° C. is introduced into the gas. These effects are much more marked when the gas is under pressure and extend even to liquid acetylene.

The explosion of a mixture of acetylene and air or oxygen is all the more violent owing to the endothermic character of acetylene. As the equation for the combustion is $C_2H_2 + O_5 = 2CO_2 + H_2O$, the most explosive mixture is one of 2 volumes of acetylene and 5 volumes of oxygen, or 25 volumes of air.

88. **Olefiant gas** or **ethylene** ($C_2H_4 = 28$ parts by weight).—This gas is found in larger quantity than is acetylene, among the products of the action of heat upon coal and other substances rich in carbon, and it is an important constituent of the illuminating gases obtained from such materials.

Fig. 115.—Preparation of olefiant gas.

Olefiant gas may readily be prepared by the action of strong sulphuric acid (oil of vitriol, H_2SO_4) upon alcohol (spirit of wine, C_2H_6O).

Two measures of oil of vitriol are introduced into a flask (Fig. 115), and one measure of alcohol is gradually poured in, the flask being agitated after each addition; much heat is evolved, and there would be danger in mixing large volumes suddenly.* On applying a moderate heat, the liquid darkens and effervesces and the gas may be collected in jars filled with water. When the mixture has become thick, and the evolution of the gas is slow, the end of the tube must be removed from the water and the lamp extinguished. Eighty-five c.c. of spirit of wine generally give about 8 litres of olefiant gas.

The gas will be found to have a very peculiar odour, in which that of ether and of sulphurous acid gas are perceptible. One of the jars may be closed with a glass plate, and placed upon the table with its mouth upwards; on the approach of a flame, the gas will take fire, burning with a bright white flame characteristic of olefiant gas, and seen to best advantage when, after kindling the gas, a stream of water is poured down into the jar in order to displace the gas.

Another jar of the gas may be well washed by transferring it repeatedly from one jar to another under water. a little solution of potash may then be poured into it, and the jar violently shaken, its mouth being covered with a glass plate; the potash will remove all the sulphurous acid gas, and the gas will now exhibit the peculiar faint odour which belongs to olefiant gas.

The purified gas may be transferred, under water, to another jar, kindled, and allowed to burn out; if a little lime-water be then shaken in the jar, its turbidity will indicate the presence of carbonic acid gas, which is produced together with water, when olefiant gas burns in air, $C_2H_4 + O_4 = 2CO_2 + 2H_2O$.

A somewhat better yield of gas is obtained by boiling syrupy phosphoric acid (sp. gr. 1.75) in a flask and dropping in alcohol slowly, the temperature of the mixture being kept at about 200° C.

On comparing the composition of olefiant gas (C_2H_4) with that of alcohol (C_2H_6O), it is evident that the former may be supposed to be produced from the latter by the abstraction of a molecule of water (H_2O) which is removed by the sulphuric acid, though other secondary changes occur, resulting in the separation of carbonaceous matter and

* If methylated spirit be employed, the mixture will have a dark, red-brown colour.

the production of sulphurous acid gas. A more complete explanation of the action of sulphuric acid upon alcohol must be reserved for the chemical history of this compound.

Olefiant gas derives its name from its property of uniting with chlorine and bromine to form oily liquids, a circumstance which is applied for the determination of the proportion of this gas present in coal gas, upon which part of the illuminating value of coal gas depends. The compound with chlorine ($C_2H_4Cl_2$) is known as *Dutch liquid*, having been discovered by Dutch chemists, and is remarkable for its resemblance to chloroform in odour.

To exhibit the formation of Dutch liquid, a quart cylinder (Fig. 116) is half filled with olefiant gas, and half with chlorine, which is rapidly passed up into it, from a bottle of the gas, under water. The cylinder is then closed with a glass plate, and supported with its mouth downwards under water in a *separating funnel*, furnished with a glass stop-cock. The volume of the mixed gases begins to diminish immediately, drops of oil being formed upon the side of the cylinder and the surface of the water. As the drops increase, they fall to the bottom of the funnel. Water must be poured into the funnel to make good that which rises into the cylinder, and when the whole of the gas has disappeared, the oil may be drawn out of the funnel through the stop-cock into a test-tube, in which it is shaken with a little potash to absorb any excess of chlorine. The fragrant odour of the Dutch liquid will then be perceived, especially on pouring it out into a shallow dish.

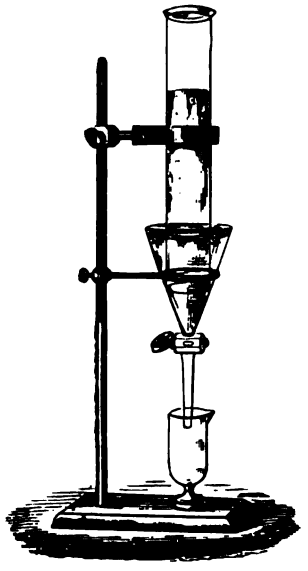


Fig. 116.

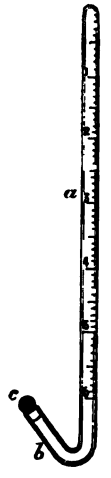


Fig. 117.

In applying this principle to the measurement of the illuminating hydrocarbons in coal gas, daylight must be excluded, or an error would be caused by the union of the free hydrogen with the chlorine or bromine. The *bromine test* may be applied in the tube represented in Fig. 117. The gas to be examined is measured over water in the divided limb *a*, with due attention to temperature and pressure: the tube being held perpendicularly, the limb *b* will remain filled with water, so that gas cannot escape nor air enter. A drop or two of bromine is poured into this limb, which is then depressed beneath the water in the pneumatic trough, and closed by the stopper *c*. On shaking the gas with the water and bromine, the latter will absorb the illuminating hydrocarbons; and if the tube be again opened under water, the volume of the gas in *a* will be found to have diminished, and the diminution gives an approximate estimate of the olefiant gas and other illuminating hydrocarbons.

A very instructive experiment consists in filling a three-pint cylinder one-third full of olefiant gas, then rapidly filling it up, under water, with two pints of chlorine, closing its mouth with a glass plate, shaking it to mix the gases, slipping the plate aside and applying a light, when the mixture burns with a red flame which passes gradually down the cylinder, and is due to the combination of the hydrogen with the chlorine, the whole of the carbon being separated in the solid state—$C_2H_4 + Cl_4 = 4HCl + C_2$.

When olefiant gas is subjected to the action of high temperatures, as

by passing through heated tubes, one portion is decomposed into marsh gas (CH_4) with separation of carbon, acetylene (C_2H_2) and hydrogen being also produced; this decomposition will be found to be of great importance in the manufacture of coal gas.

The action of heat upon olefiant gas is most conveniently shown by exposing it to the spark from an induction-coil in the apparatus shown in Fig. 67.

The carbon separated during the sparking sometimes forms a conducting communication, and allows the current to pass without a spark. This may be obviated by reversing the current, or by gently shaking the tube.

The olefiant gas will expand to nearly twice its former volume.

To show the production of acetylene, another arrangement may be found convenient (Fig. 118). A globe with four necks is employed; through two of these necks are passed, airtight with perforated corks, the copper wires connected with the induction-coil. A third neck receives a tube, conveying olefiant gas from a gas-holder, whilst from the fourth proceeds a tube dipping to the bottom of a small cylinder. When the whole of the air has been displaced by olefiant gas, a solution of cuprous chloride in ammonia is poured into the cylinder, and the gas allowed to bubble through it, when the absence of acetylene will be shown by there being no red compound formed. As soon, however, as the spark is passed, the red precipitate will appear, and in a very few minutes a large quantity will be deposited. Coal gas may be employed instead of olefiant gas, but of course a smaller quantity of the copper compound will be obtained.

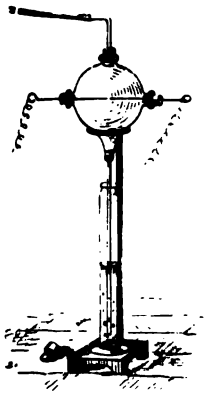


Fig. 118.—Preparation of cuprous acetylide from olefiant gas.

89. **Marsh gas, methane,** or ***light carburetted hydrogen*** ($CH_4 = 16$ parts by weight). This hydrocarbon is found in nature, being produced wherever vegetable matter is undergoing decomposition in the presence of moisture. The bubbles rising from stagnant pools, when collected and examined, are found to contain marsh gas mixed with carbonic acid gas, and there is reason to believe that these two gases represent the principal forms in which the hydrogen and oxygen respectively were separated from wood during the process of its conversion into coal. This would account for the constant presence of marsh gas in the coal formations, where it is usually termed *fire-damp*. It is occasionally found pent up under pressure between the layers of coal, and the pores of the latter are sometimes so full of it that it may be seen rising in bubbles when the freshly hewn coal is thrown into water. Perhaps a similar origin is to be ascribed to the liquid hydrocarbons chemically similar to marsh gas, which are found so abundantly in Pennsylvania and Canada, and are known by the general name of *petroleum*. From certain gas-springs in Pennsylvania, marsh gas, olefiant gas, and ethane, C_2H_6, are discharged at very high pressure, and are employed for heating and lighting.

Marsh gas is obtained artificially by the following process:

35 grams of dried sodium acetate are finely powdered and mixed, in a mortar, with 35 grams of the mixture of calcium hydroxide and sodium hydroxide, which is sold as *soda-lime*. The mixture is heated in a Florence flask (or better a copper tube, for the alkali corrodes the glass) and the gas collected over water.

The decomposition will be evident from the following equation:—

$$\underset{\text{Sodium acetate.}}{NaC_2H_3O_2} + \underset{\text{Caustic soda.}}{NaOH} = \underset{\text{Sodium carbonate.}}{Na_2CO_3} + CH_4.$$

The marsh gas will be easily recognised by its burning with a pale illuminating

flame, far inferior in brilliancy to those of olefiant gas and acetylene, but unattended with smoke.*

By heating a mixture of alumina and carbon in the electric furnace, *aluminium carbide*, Al_4C_3, is obtained. This is decomposed by water yielding methane just as calcium carbide yields acetylene—$Al_4C_3 + 12H_2O = 3CH_4 + 4Al(OH)_3$ (aluminium hydroxide).

The properties of this gas deserve a careful study, on account of the frequent fatal explosions to which it gives rise in coal-mines, where it is often found accumulated under pressure, and discharging itself with considerable force from the fissures or *blowers* made in hewing the coal. March gas has no characteristic smell like that of coal gas, and the miner thence receives no timely warning of its presence; it is much lighter than air (sp. gr. 0.5596), and therefore very readily diffuses itself (page 25) through the air of the mine, with which it forms an explosive mixture as soon as it amounts to one-fourteenth of the volume of the air. The gas issuing from the blower would burn quietly on the application of a light, since the marsh gas is not explosive unless mixed with the air, when a large volume of the gas is burnt in an instant, causing a sudden evolution of a great deal of heat, and a consequent sudden expansion or explosion exerting great mechanical force. The most violent explosion occurs when 1 volume of marsh gas is mixed with 2 volumes of oxygen, since this quantity is exactly sufficient to effect the complete combustion of the carbon and hydrogen of the gas, and therefore to evolve the greatest amount of heat: $CH_4 + O_4 = CO_2 + 2H_2O$. The calculated pressure exerted by the exploding mixture of marsh gas and oxygen amounts to 37 atmospheres, or 555 lbs. upon the square inch. Since air contains one-fifth of its volume of oxygen, it would be necessary to employ 10 volumes of air to 1 volume of marsh gas in order to obtain perfect combustion, but the explosion will be much less violent on account of the presence of the 8 volumes of inert nitrogen, the calculated pressure exerted by the explosion being only 14 atmospheres, or 210 lbs. on the square inch. Of course, if more air be employed, the explosion will be proportionally weaker, until, when there are more than 14 volumes of air to each volume of marsh gas, the mixture will be no longer explosive, but will burn with a pale flame around a taper immersed in it. The severity of the explosion of a gaseous mixture depends on the rate at which the chemical combination proceeds throughout the mixture. If, on a certain number of particles combining, the heat evolved has to be shared between the neighbouring combustible particles and a number of inert particles the temperature of the former may not rise to the ignition point, whereupon propagation of the combination ceases. It must be remembered that an excess of either of the reacting gases also serves as an inert gas. Hence in every explosive mixture there is an upper limit and a lower limit to the proportion of the constituents, and it is only between these limits that explosion occurs. In the case of methane and air the explosion only occurs if the methane is mixed with between 6 and 14 times its volume of air. The carbonic acid gas resulting from the explosion is called by miners the *after-damp*, and its effects are generally fatal to those who may have escaped death from the explosion itself.

Coal gas, which contains much hydrogen, requires a smaller volume

* The gas prepared by the above process contains acetone, which increases its luminosity. For the preparation of pure marsh gas, see *Organic Chemistry*.

of air than does marsh gas to render it explosive. With 16-candle gas, such as is used in London, 6 volumes of air to 1 volume of gas would give the most powerful explosion, and the limits are about 3.5 and 14 volumes of air.

Fortunately, marsh gas requires a much higher temperature to inflame it than most other inflammable gases; a solid body at an ordinary red heat does not kindle the gas unless kept in contact with it for a considerable period; contact with flame, or with a body heated to whiteness, being required to ignite it instantaneously.

If two strong gas cylinders be filled, respectively, with mixtures of 2 volumes hydrogen and 1 volume oxygen, and of 1 volume marsh gas and 2 volumes oxygen, it will be found, on holding them with their mouths downwards, and inserting a red-hot iron bar that the marsh gas mixture will not explode, but if the bar be transferred at once to the hydrogen mixture there will be an explosion. A lighted taper may then be used to explode the marsh gas and oxygen.

In consequence of the high temperature required to inflame the mixture of marsh gas and air, it is necessary that the mixture be allowed to remain for an appreciable time in contact with the flame before its particles are raised to the igniting-point. It was on this principle that Stephenson's original safety-lamp was constructed, the flame being surrounded with a tall glass chimney, the rapid draught through which caused the explosive mixture to be hurried past the flame without igniting.

To illustrate this, a copper funnel holding about two quarts is employed, the neck of which has an opening of about ¼ inch in diameter. The funnel being placed mouth downwards in the pneumatic trough, the orifice is closed with the finger, and a half-pint of coal gas passed up into the funnel. The latter is now raised from the water, so that it may become entirely filled with air. By depressing the funnel to a considerable depth in the water, the aperture being still closed by the finger, the mixture will be confined under considerable pressure, and if a lighted taper be held to the aperture, and the finger removed, it will be found that the mixture sweeps past the flame without exploding, until the water has reached the same level in the funnel as in the trough, when the gas comes to rest and explodes with great violence.

Fig. 119.

Davy's safety lamp (Fig. 120) is an application of the principle that ignited gas (*flame*) is extinguished by contact with a large surface of a good conductor of heat, such as copper or iron.

If a thin copper wire be coiled round into a helix, and carefully placed over the wick of a burning taper (Fig. 121), the flame will be at once extinguished, its heat being so rapidly transmitted along the wire that the temperature falls below the point at which the combustible gases enter into combination with oxygen, and therefore the combustion ceases. If the coil be heated to redness in a spirit-lamp flame before being placed over the wick, it will not abstract the heat so readily, and will not extinguish the flame. If a copper tube were substituted for the coiled wire, the same result would be obtained, and by employing a number of tubes of very small diameter, so that the metallic surface may be very large in proportion to the volume of ignited gas, the most energetic combustion may be arrested, a fact of which advantage is taken in the oxy-hydrogen blow-pipe (p. 48). It is evident that the exposure of a large extent of cooling surface to the action of the flame may be

effected either by increasing the length or by diminishing the width of the metallic tubes, so that wire gauze, which may be regarded as a collection of very short tubes, will form an effectual barrier to flame, provided that it has a sufficient number of meshes to the inch.

If a piece of iron wire gauze, containing about 400 meshes to the square inch, be depressed upon a flame, it will extinguish that portion with which it is in contact, and the combustible gas which escapes through the gauze may be kindled by a lighted match held on the upper side. By holding the gauze 2 or 3 inches

Fig. 120.

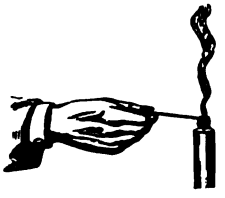


Fig. 121.

Fig. 122.

above a gas jet, the gas may be lighted above it without communicating the flame to the burner itself.

When blazing spirit is poured upon a piece of wire gauze (Fig. 122), the flame will remain upon the gauze, and the extinguished spirit will pass through. A little benzene or turpentine may be added to the spirit, so that its flame may be more visible at a distance.

The safety lamp (Fig. 120) is an oil lamp, the flame of which is surrounded by a cage of iron wire gauze, having 700 or 800 meshes in the square inch, and made double at the top, where the heat of the flame chiefly plays. This cage is protected by stout iron wires attached to a ring for suspending the lamp. A brass tube passes up through the oil reservoir, and in this there slides, with considerable friction, a wire bent at the top, so that the wick may be trimmed without taking off the cage. The lower part of the cage is now made of glass, to afford more light.

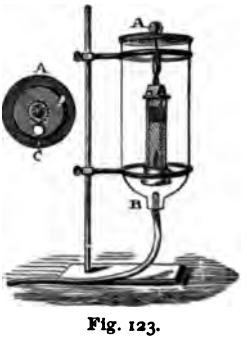


Fig. 123.

If this lamp be suspended in a large jar, closed at the top with a perforated wooden cover A (Fig. 123), and having an aperture (B) below, through which coal gas is allowed to pass slowly into the jar, the flame will be seen to waver, to elongate very considerably, and to be ultimately extinguished, when the wire cage will be filled with a mixture of coal gas and air burning tranquilly within the gauze, which prevents the flame from passing to ignite the explosive atmosphere surrounding the lamp: that an explosive mixture really fills the jar may be readily ascertained by introducing through an aperture (C) in the cover, the unprotected flame of a taper, when an explosion will occur.

This experiment illustrates the action of the Davy lamp in a mine which contains fire-damp. It would obviously be unsafe to allow the lamp to remain in the explosive mixture when the cage is filled with flame, for the gauze would either become sufficiently heated to kindle the surrounding gas, or would be oxidised and eaten into holes, which would allow the passage of the flame. Nor should the lamp be exposed to a very strong draught, which might possibly be able to carry the flame through the meshes.

When the Davy lamp is brought into an atmosphere containing fire-damp, a "cap" of blue flame is observed to play above the tip of the illuminating flame.

This incipient combustion is more marked when a hydrogen flame is substituted for an oil flame, and the height of the cap furnishes an indication of the quantity of fire-damp present. Such a modified Davy lamp becomes a fire-damp indicator, showing as little as 0.25 per cent.

All coal contains a considerable quantity of gas *occluded* or condensed in its pores, part of which issues when the surface of the coal is exposed, and part is retained, and can be extracted by exposure *in vacuo* and moderately heating. Bituminous coals evolve more CO_2 and N, and less CH_4, than anthracite does, hence these coals may often be worked with naked lights, while seams of steam coal and anthracite are dangerous. Cannel coal has occluded, beside the above gases, some *ethane*, C_2H_6, and Whitby jet has been found to contain *butane*, C_4H_{10}. The gas from *blowers* sometimes contains 97 per cent. by volume of marsh gas, with a little CO_2 and N.

Whenever naked flames are used in the mine, there must always be great risk; in most seams of coal there are considerable accumulations of fire-damp; when a fissure is made, the gas escapes very rapidly from the *blower*, and the air in its vicinity may soon become converted into an explosive mixture. In mines where small quantities of fire-damp are known to be continually escaping from the coal, ventilation is depended upon in order to dilute the gas with so large a volume of air that it is no longer explosive, and finally to sweep it out of the mine; but it has occasionally happened that the ventilation has been interfered with by a door having been left open in one of the galleries, or by a passage having been obstructed through the accidental falling in of a portion of the coal, and an explosive mixture has then been formed.

The presence of fine dust of coal in the air of the mine greatly increases the liability to explosion; indeed, there is no doubt that in some cases the dust has been the sole cause of the explosion. Most combustible substances mixed in a finely divided state with air, burn so rapidly as to produce effects of explosion. Flour mills have been destroyed from this cause in very dry weather.

If some *lycopodium*, the seed of the club-moss, sometimes called *vegetable brimstone*, be placed in a glass funnel, the stem of which has been lightly stopped with wool, and has two or three feet of wide vulcanised tubing attached to it, the lycopodium may be blown out in a cloud by a sudden puff of air, and if a lighted taper be held in the cloud, an immense volume of flame may be formed.

Explosions in dusty mines are more common when gunpowder is used for blasting than when the modern nitro-powders are used. This has been attributed to the considerable quantity of CO which occurs among the products of explosion of blasting gunpowder. This, or any other inflammable gas, serves to start the explosion of the dusty air.

An ingenious fire-damp indicator has been constructed of two platinum wires, which are heated by a magneto-electric current. One wire is sheltered from the fire-damp, and the other, being exposed to it, glows more strongly on account of the slow combustion of the fire-damp at the surface of the platinum (see *Platinum*). By a careful comparison of the two wires, it is said that 0.25 per cent. of marsh gas in air may be detected, whilst the Davy lamp will not indicate less than 2 per cent.

Structure of Flame.

90. The consideration of the structure and properties of ordinary flames is necessarily connected with the history of olefiant gas and marsh gas. Flame may be defined as gaseous matter heated to the temperature at which it becomes visible, or emits light. Solid particles begin, for the most part, to emit light when heated to about 500° C.; but gases, on account of their lower radiating power, must be raised to a far higher temperature, and hence the point of visibility is seldom

attained, except by gases which are themselves combustible, and therefore capable of producing, by their own combination with atmospheric oxygen, the requisite degree of heat. The presence of a combustible gas (or vapour), therefore, is one of the conditions of the existence of flame; a diamond, or a piece of thoroughly carbonised charcoal, will burn in oxygen with a steady glow, but without flame, since the carbon is not capable of conversion into vapour, while sulphur burns with a voluminous flame, in consequence of the facility with which it assumes the vaporous condition. It will be observed, moreover, that in the case of a non-volatile combustible, the combination with oxygen is confined to the surface of contact, whilst in the flame of a gas or vapour the combustion extends to a considerable depth, the oxygen intermingling with the gaseous fuel.

Flames may be conveniently spoken of as *simple* or *compound*, accordingly as they involve one or more phenomena of combustion; thus, for example, the flames of hydrogen and carbonic oxide are simple, whilst those of marsh gas, olefiant gas, and hydrocarbons generally, are compound, since they involve both the conversion of hydrogen into water and of carbon into carbon dioxide.

It is obvious that simple flames must be hollow in ordinary cases, such as that of a gas issuing from a tube into the air, the hollow being occupied by the combustible gas to which the oxygen does not penetrate.

All the flames which are ordinarily turned to useful account are compound flames, and involve several distinct phenomena. Before examining these more particularly, it will be advantageous to point out the conditions which regulate the luminosity of flames.

In order that a flame may emit a brilliant light, it is essential that it should contain particles which, either from their own nature or from the conditions under which they are placed, do not admit of very much expansion by the heat of the flame, but are capable of being heated to *incandescence*. Thus the flame of the oxyhydrogen blowpipe (p. 48) emits a very pale light, but if the mixture of oxygen and hydrogen be restrained from expanding when fired, as in the Cavendish eudiometer, it gives a bright flash; or if the flame be directed upon some solid body little affected by the heat, such as lime, the light is very intense.

Phosphorus and arsenic burn with very luminous flames, in consequence of the formation of very dense vapours of phosphoric and arsenious oxides during the combustion; the density of the vapours being here attended with the same result as that produced by the restrained expansion of the steam formed in the Cavendish eudiometer.

It is not necessary that the incandescent matter should be a product of the combustion; any extraneous solid in a finely divided state will confer illuminating power upon a flame. Thus, the flame of hydrogen may be rendered highly luminous by blowing a little very fine charcoal powder into it.

The luminosity of all ordinary flames is due to the presence of highly heated carbon in a state of very minute division, and it remains to consider the changes by which this finely divided carbon is separated in the flame.

A candle, a lamp, and a gas-burner exhibit contrivances for procuring light artificially in different degrees of complexity, the candle being the

most complex of the three. When a new candle is lighted, the first portion of the wick is burnt away until the heat reaches that part which is saturated with the wax or tallow of which the candle is composed; this wax or tallow then undergoes destructive distillation, yielding a variety of products, among which olefiant gas is found in abundance. The flame furnished by the combustion of these products melts the fuel around the base of the wick, through which it then mounts by capillary attraction, to be decomposed in its turn, and to furnish fresh gases for the maintenance of the flame. In a lamp, the fuel being liquid at the commencement, the process of fusion is dispensed with; and in a gas-burner, where the fuel is supplied in a gaseous form, the process of destructive distillation has been already effected at a distance. It will be seen, however, that the final result is similar in all three cases, the flame being maintained by such gases as hydrogen, acetylene, marsh gas, and olefiant gas arising from the destructive distillation of wax, tallow, oil, coal, &c.

The shape of the candle flame is common to all flames which consist of gas issuing from a small circular jet, like the wick of the candle. The gas issues from the jet in the form of a cylinder, which, however, immediately becomes a diverging cone by diffusing into the surrounding air. When this cone is kindled, the margin of it, where intermixture with the surrounding air is most complete, will be perfectly burnt, but the gases in the interior of the diverging cone cannot burn until they have ascended sufficiently to meet with fresh air; since these unburnt gases are continually diminishing in quantity, the successive circles of combustion must diminish in diameter and the conical shape is the only possible form.

Fig. 124.

On examining an ordinary flame—that of a candle, for instance—it is seen to consist of three concentric

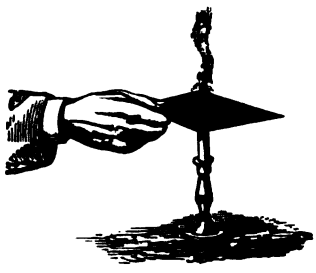


Fig. 125.

cones (Fig. 124), the innermost, around the wick, appearing almost black, the next emitting a bright white light, and the outermost being so pale as to be scarcely visible in broad daylight. There is also apparent a bright blue cup surrounding the base of the flame.

The dark innermost cone consists merely of the gaseous combustible to which the air does not penetrate, and which therefore is not in a state of combustion.

The nature of this cone is easily shown by experiment: a strip of cardboard held across the flame near its base will not burn in the centre where it traverses the innermost cone; a piece of wire gauze depressed upon the flame near the wick (Fig. 125) will allow the passage of the combustible gas, which may be kindled above it. The gas may be conveyed out of the flame by means of a glass tube, inserted into the innermost cone, and may be kindled at the other extremity of the tube, which should be inclined downwards (Fig. 126).

A piece of phosphorus in a small spoon held in the interior of the flame of a spirit-lamp will melt and boil, but will not burn unless it be removed from the flame, and may then be extinguished by replacing it in the flame.

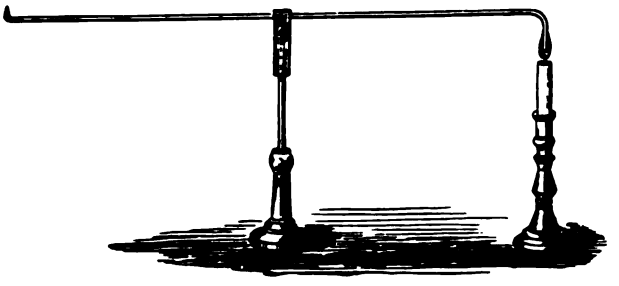


Fig. 126.

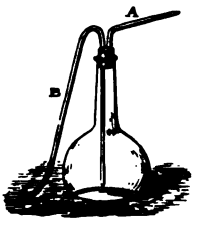


Fig. 127.

The combustible gas from the interior of a flame may be collected in a flask (Fig. 127) furnished with two tubes, one of which (A) is drawn out to a point for insertion into the flame, whilst the other (B), which passes to the bottom of the flask, is bent over and prolonged by a piece of vulcanised tubing so that it may act as a siphon. The flask is filled up with water, the jet inserted into the interior of a flame, and the siphon set running by exhausting it with the mouth. As the water flows out through the siphon, the gas is drawn into the flask, and after removing the tube from the flame, the gas may be expelled by blowing down the siphon tube, and may be burnt at the jet. When a candle is used for this experiment, some solid products of destructive distillation will be found condensed in the flask.

In the second or luminous cone, combustion is proceeding, but it is by no means perfect, being attended by the separation of a quantity of carbon, which confers luminosity upon this part of the flame. The presence of free carbon is shown by depressing a piece of porcelain upon this cone, when a black film of soot is deposited. The liberation of the carbon is due to the decomposition of the hydrocarbons by the heat, which separates the carbon from the hydrogen,* and this latter undergoing combustion evolves sufficient heat to raise the separated carbon to a white heat, the supply of air which penetrates into this portion of the flame being insufficient to effect the combustion of the whole of the carbon.

According to Lewes the temperature of the innermost cone of a hydrocarbon flame rises to about 1000° C. near the apex of the cone. This temperature is sufficiently high to decompose the heavier hydrocarbons into acetylene. This acetylene is decomposed, with liberation of carbon, in the luminous cone where the temperature rises to 1300° C., owing to the combustion of the carbon monoxide and hydrogen, the former produced by the imperfect oxidation, and the latter by the decomposition, of the hydrocarbons in the innermost cone.

Some very simple experiments will illustrate the nature of the luminous portion of flame.

* The action of heat on hydrocarbons is to break them down, or "crack" them, into such as contain a higher percentage of carbon; these, in their turn, are decomposed with liberation of carbon at very high temperatures.

Over an ordinary candle flame (Fig. 128) a tube may be adjusted so as to convey the finely divided carbon from the luminous part of the flame into the flame of hydrogen, which will thus be rendered as luminous as the candle flame, the dark colour of the carbon being apparent in its passage through the tube.

One of the limbs of the U tube (Fig. 129) contains a tuft of cotton wool *b*. On kindling the hydrogen supplied through *c* at the orifice of each tube, no difference will be seen in the flames until a drop of benzene (C_6H_6) is placed upon the cotton, when its vapour, mingling with the hydrogen, will furnish enough carbon to render the flame brilliantly luminous.

The pale outermost cone, or *mantle*, of the flame, in which the separated carbon is finally consumed, may be termed the cone of perfect combustion, and is much thinner than the luminous cone, the supply of air to this external shell of flame being unlimited, and the combustion therefore speedily effected.

The bright blue cup surrounding the base of the flame is formed by the perfect combustion (without any separation of carbon) of a small

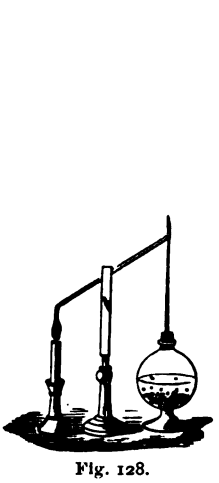


Fig. 128.

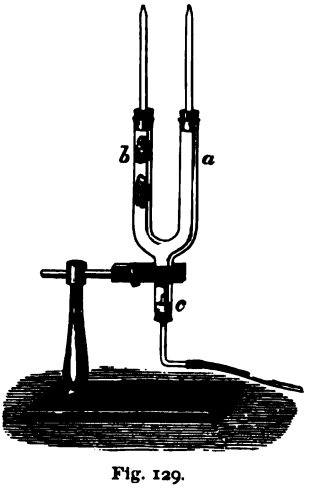


Fig. 129.

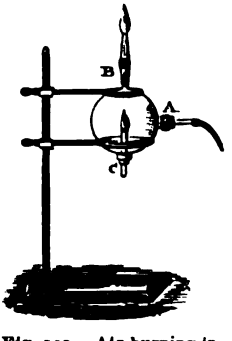


Fig. 130.—Air burning in coal gas.

portion of the hydrocarbons owing to the complete admixture of air at this point.

The mantle of the flame may be rendered more visible by burning a little sodium near the flame, when the mantle is tinged strongly yellow.

According to another view, based on the observation that acetylene—a constant product of checked combustion—can be discovered in the products of the combustion of a hydrocarbon flame burning under ordinary conditions, the mantle is a thin layer of the flame rendered non-luminous by admixture with the surrounding air, the cooling effect of which gradually quenches the combustion.

By means of a siphon about one-third of an inch in diameter, the nature of the different portions of an ordinary candle flame may be very elegantly shown. If the orifice of the siphon be brought just over the extremity of the wick, the combustible gases and vapours will pass through it, and may be collected in a small flask, where they can be kindled by a taper. On raising the orifice into the luminous portion of the flame, voluminous clouds of black smoke will pour over into the flask, and if the siphon be now raised a little above the point of the flame, carbonic acid gas can be collected in the flask, and may be recognised by shaking with lime-water.

The reciprocal nature of the relation between the combustible gas and the air

which supports its combustion may be illustrated in a striking manner by burning a jet of air in an atmosphere of coal gas.

A quart glass globe with three necks is connected at A (Fig. 130) with the gaspipe by a vulcanised tube. The second neck (B), at the upper part of the globe, is connected by a short piece of vulcanised tube with a piece of glass tube about ½ inch wide, from which the gas may be burnt. Into the third and lowermost neck is inserted, by means of a cork, a thin brass tube C (an old cork-borer), about ¼ inch in diameter. When the gas is turned on, it may be lighted at the upper neck ; and if a lighted match be then quickly thrust up the tube C, the air which enters it will take fire, and burn inside the globe.

A simple experiment to show the burning of gas in air may be made with an Argand burner (Fig. 131). The flame having been turned low, a dish (or dial-glass containing water to prevent cracking) is placed so as to close the top of the chimney, when the gas flame will be extinguished, and the air which enters the inner circle will burn with a pale flame, which may be made more visible by thrusting up a copper wire dipped in hydrochloric acid. A bottomless beaker makes a good chimney for this purpose.

An interesting confirmation of the above views as to the structure of an illuminating flame is furnished by observing what occurs when the rate at which the gaseous combustible is supplied to the flame is very gradually increased, either by kindling a candle the wick of which has been cut short, or by slowly increasing the gas supply to an ordinary burner. When the flame is very small it is seen to consist of a bright blue inner cone surrounded by a pale lilac mantle. The bright blue cone is an area of combustion where there is sufficient air to burn the hydrocarbons to gaseous products, without separation of carbon, but not sufficient to burn them completely to CO_2 and H_2O. It has been shown that under these conditions much of the carbon in the hydrocarbons burns to carbon monoxide, and only a part of the hydrogen is burnt. The CO and H escape from the inner cone and burn when they come in contact with more air, forming the mantle. As the supply of gas is increased a luminous spot becomes visible, and gradually increases in area until it becomes the luminous cone, at the same time the core of unburnt gas makes its appearance. What was at first the inner blue cone now becomes the bright blue cup at the base of the flame, and the mantle remains. The advent of the luminous spot indicates that the quantity of gas has so far increased that there is now insufficient air to burn the carbon separated from the hydrocarbons by the heat of the flame.

The luminosity of a flame is materially affected by the pressure of the atmosphere in which it burns, a diminution of pressure causing a loss of illuminating power. If the light of a given flame burning in the air when the barometer stands at 30 inches be represented by 100, each diminution of 1 inch in the height of the barometer will reduce the luminosity by 5 ; and, conversely, when the barometer rises 1 inch, the luminosity will be increased by 5. This is not due to any difference in the rate of burning, which remains pretty constant, but to the more complete impenetration of the rarefied air and the gases composing the flame ; this gives rise to the separation of a smaller quantity of incandescent carbon. In air at a pressure of 120 inches of mercury, the flame of alcohol is highly luminous.

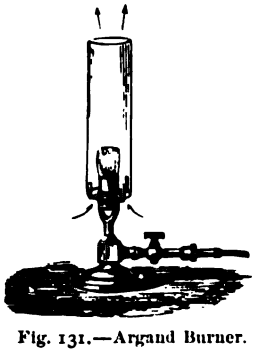


Fig. 131.—Argand Burner.

From this review of the structure of flame, it is evident that, in order to secure a flame which shall be useful for illumination, attention must be paid to the supply of oxygen (or air), and to the composition of the fuel employed. Much attention has been paid to the construction of burners which, by causing the illuminant to issue into the air at a rate and in a shape best suited to the production of lighting effect, shall give the most economical result, that is, the highest illuminating value (*candle power*) per unit of combustible. The use of the chimney of an Argand burner (Fig. 132) affords an instance of the necessity for attention to the proper supply

of air. Without the chimney, the flame is red at the edges and smoky, for the supply of air is not sufficient to consume the whole of the carbon which is separated, and the temperature is not competent to raise it to a bright white heat, defects which are remedied as soon as the chimney is placed over it and the rapidly ascending heated column of air draws in a liberal supply beneath the burner, as indicated by the arrows.

By using two chimneys, and causing the air to pass down between them, so as to be heated before reaching the flame, and to be less capable of chilling the flame, an equal amount of light may be obtained from a much smaller supply of gas; this is the principle underlying the *regenerative burner*.

The importance of the chemistry of illuminating flames has, however, much diminished during the past few years owing to the perfection to which the system of illumination first put on a practical basis by Welsbach, has been brought. Whereas in an illuminating flame the combustible supplies not only the heat required to raise a dense substance to the temperature at which it can emit light, but also the dense substance (carbon) itself, under the Welsbach or Auer system the sole function of the combustible is to supply heat, the dense substance being an incombustible material suspended in the flame. Hence the principle of the system is the same as that of the Drummond light (p. 48) known many years before Welsbach.

Since a luminous flame contains carbon in a condition in which it is very readily deposited on any surface held in the flame, it is desirable that a gas burner which is to be used for heating, whether for producing light or for any other purpose, should supply a non-luminous flame. A deposit of soot forms a non-conducting layer through which the heat travels slowly; moreover, every particle of soot which escapes combustion signifies a loss in the calorific power of the gas. The smokeless gas burners employed in laboratories and kitchens exhibit the result of mixing the gas with a considerable proportion of air before burning it, the luminous part of the flame then entirely disappearing, because there is sufficient oxygen in the flame to burn the hydrocarbons before they can be decomposed with separation of carbon. By careful adjustment of the supply of air the combustion can be made to take place in a smaller space than when the gas has to seek its air supply from the surrounding atmosphere. For the same amount of gas consumed, that flame which is the smaller will have the higher temperature, although it must be understood that the same amount of *heat* is produced from a given volume of gas, however it is burnt, provided that the combustion is complete, *i.e.*, that the products are only CO_2 and H_2O.

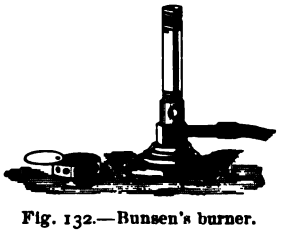


Fig. 132.—Bunsen's burner.

The principle upon which all air-gas burners are constructed is illustrated by *Bunsen's burner* (Fig. 132), in which the gas is conveyed through a narrow jet into a wide tube, at the base of which are two large holes for the admission of air. When a good supply of gas is turned on, a quantity of air, about $2\frac{1}{2}$ times the volume of the gas, is drawn in through the lower apertures, and the mixture of air and gas

may be kindled at the orifice of the wide tube, its rapid motion preventing the flame from passing down the tube. By closing the air-holes with the fingers, a luminous flame is at once produced.

The luminosity of the flame may also be destroyed by supplying nitrogen instead of air to the Bunsen burner, when the diminution of the light is partly due to the increased area of the flame and partly to the cooling effect of the nitrogen, by which the temperature is lowered below that at which the hydrocarbons are decomposed with separation of carbon. This cooling effect occurs to some extent when air is supplied to the burner; the nitrogen in this air lowers the temperature of the flame just at that point where, in a luminous flame, the hydrocarbons are decomposed, although the more perfect combustion makes the temperature in other portions of the non-luminous flame higher than at corresponding points of the luminous flame. When the air and coal gas are heated before being supplied to the burner the cooling effect of the nitrogen is counteracted, and the flame becomes luminous. The ordinary Bunsen flame consists of only two cones; the inner one is a core of mixture of air and gas which cannot be kindled because its rate of passage is more rapid than the rate at which a flame can travel in it; the combustion occurs in the outer cone, where the speed has diminished.

When the gas supply to a Bunsen burner is checked, the velocity of issue of the mixture of air and gas becomes so far diminished that it is no longer greater than the rate at which the flame can travel in the mixture, consequently the flame passes down the tube of the burner and burns at the jet from which the coal-gas issues; here the checked combustion will give rise to much acetylene, detected by its odour. By slipping a glass tube, some three or four feet long, over the tube of the burner, taking care not to cover the air inlet, and kindling the gas at the orifice of this tube, the flashing back of the flame may be observed. If the glass tube be constricted at a point some foot or so away from the orifice, the descending flame will be stopped at this constriction, for here the velocity of issue will be again sufficiently great to prevent further flashing back. Inasmuch as the flame at the constriction is burning out of contact with surrounding air, only such products are formed by its combustion as can be produced by the action of the oxygen supplied in the air from the burner; these include much CO and H, so that a second flame composed of these gases burning in the air will generally be seen at the orifice of the tube. A more elaborate apparatus for showing this experiment is seen in Fig. 133; in this the height of the constriction can be varied by sliding the outer tube on the rubber rings A A. Air and gas are supplied through the T-piece.

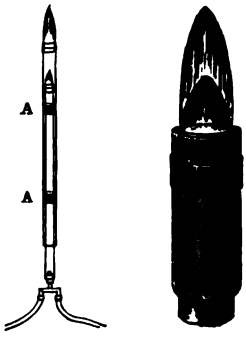


Fig. 133.

The Welsbach *mantle* is a skeleton of the highly infusible oxide of thorium containing about 1 per cent. of oxide of cerium. This mixture has a remarkable power of converting the heat energy of the burning gas into light energy,* and when the mantle is suspended in a suitable air-gas flame it produces light at about one-fifth the cost for gas that is involved if the same gas is burnt as a luminous flame.

The Welsbach mantle is made by soaking in a solution containing the nitrates of thorium and cerium, and generally ammonium nitrate, a knitted cylinder of cotton thread, drawn together by an asbestos thread at one end. After drying, the cotton is ignited and allowed to burn away, leaving the mineral matter in the exact form of the original cotton thread. The mantle is then heated very strongly to "harden" it, and dipped in a solution of collodion to stiffen it for the market; when it is placed on the burner and the gas is kindled the film of collodion rapidly burns away.

The air-gas burner for the Welsbach light is constructed in such a manner that the mixture of air and gas issuing from the burner is nearly in the proper propor-

* It is claimed that as much as 25 per cent. is converted.

tion for complete combustion; that is to say, the mixture should be "self-burning," requiring little or none of the surrounding air. In this manner the hottest attainable flame is produced. The burner generally has the form of the frusta of two cones, the upper inverted on the lower; the gas issues as a jet into the lower cone and draws in some four or five times its volume of air. The orifice of the burner tube must be covered with wire gauze to prevent the flame from flashing back. The flame of a burner of this kind is characterised by the inner cone having a much greener appearance than has that of the ordinary Bunsen flame. The temperature of the hottest portion of the ordinary Bunsen flame, the centre of the outer cone, is stated to be about 1500° C., whilst at the same point in this "solid" flame the temperature is said to be about 1600° C. Fig. 134 shows an Argand burner converted into such a *gauze burner* by a covering of wire gauze. When this is placed over the gas burner, a supply of air is drawn in at the bottom by the ascending stream of gas, and the mixture burns above the gauze with a very hot smokeless flame, the metallic meshes preventing the flame from passing down to the gas below.

The candle power of the Welsbach light is about 18 per cubic foot of gas per hour, whilst that of a flat flame is between 2 and 3 on the same basis.

Fig. 134.—Gauze burner.

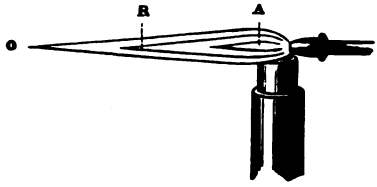


Fig. 135.—Blowpipe flame.

91. *The blowpipe flame.*—The principles already laid down will render the structure of the blowpipe flame easily intelligible. It must be remembered that in using the blowpipe, the stream of air is not propelled from the lungs of the operator (where a great part of its oxygen would have been consumed), but simply from the mouth, by the action of the muscles of the cheeks. The first apparent effect upon the flame is entirely to destroy its luminosity, the free supply of air effecting the immediate combustion of the carbon. The size of the flame, moreover, is much diminished, and the combustion being concentrated into a smaller space, the temperature must be much higher at any given point of the flame. In structure, the blowpipe flame is similar to the ordinary flame, consisting of three distinct cones, the innermost of which (A, Fig. 135) is filled with the cool mixture of air and combustible gas. The second cone, especially at its point (R), is termed the *reducing* flame, for the supply of oxygen at that part is not sufficient to convert the carbon into carbon dioxide, but leaves it as carbonic oxide, which speedily reduces almost all metallic oxides placed in that part of the flame to the metallic state. The outermost cone (O) is called the *oxidising* flame, for there the supply of oxygen from the surrounding air is unlimited, and any substance prone to combine with oxygen at a high temperature is oxidised when exposed to the action of that portion of the flame: the hottest point of the blowpipe flame, where neither fuel nor oxygen is in excess, appears to be a very little in advance of the extremity of the second (reducing) cone. The difference in the operation of the two flames is readily shown by placing a little red lead (oxide of lead) in a shallow cavity scooped upon the surface of a piece of charcoal (Fig. 136), and directing the flames upon it in succession);

the inner flame will reduce a globule of metallic lead, which may be reconverted into oxide by exposing it to the outer flame.*

Fig. 136.—Reduction of metals on charcoal.

The immense service rendered by this instrument to the chemist and mineralogist is well known.

By forcing a stream of oxygen through a flame, from a gas-holder or bag, an intensely hot blowpipe flame is obtained, in which pipeclay and platinum may be melted, and iron burns with great brilliancy.

Fletcher's *hot-blast blowpipe* (Fig. 137) produces a much higher temperature than the ordinary blowpipe. Coal gas is supplied through the tube *g*, and is kindled at the Bunsen burners *b b* and at the orifice *f*, the supply to the former being regulated by the stop-cock *c*, and to the latter by the stop-cock *d*. The flames of the Bunsen burners heat the spiral copper tube *e* to redness, so that the air blown in through the flexible tube *a* is strongly heated before being projected into the flame through a blowpipe jet at *f*. Thin platinum wires melt easily in this flame, and thin iron wires burn away rapidly.

Fig. 137.—Hot-blast blowpipe.

92. *Determination of the composition of gases containing carbon and hydrogen.*—In order to ascertain the proportions of carbon and hydrogen present in a gas, a measured volume of the gas is mixed with an excess of oxygen, the volume of the mixture carefully noted, and explosion determined by passing the electric spark; the gas remaining after the explosion is measured and shaken with potash, which absorbs the carbonic acid gas, from the volume of which the proportion of carbon may be calculated. For example,

4 c.c. of marsh gas, mixed with
10 „ oxygen, and exploded, left
6 „ gas; shaken with potash, it left
2 „ oxygen,

showing that 4 c.c. of carbonic acid gas had been produced. This quantity would contain 4 c.c. of oxygen. Deducting this last from the total amount of oxygen consumed (8 c.c.), we have 4 c.c. for the volume of oxygen consumed by the hydrogen. Now, 4 c.c. of oxygen would combine with 8 c.c. of hydrogen, which represents therefore the amount of hydrogen in the marsh gas employed. It has thus been ascertained that the marsh gas contains twice its volume of hydrogen.

The method by which the composition by weight of a gas containing

* By directing the reducing flame upon the metallic oxide in the cavity, and allowing the oxidising flame to sweep over the surface of the charcoal, as shown in the figure, a yellow *incrustation* of oxide of lead is formed upon the surface of the charcoal, which affords additional evidence of the nature of the metal.

carbon and hydrogen can be ascertained will be appreciated when the section on *ultimate organic analysis* has been studied. In the case of marsh gas such an analysis shows that the carbon and hydrogen are present in the gas in the proportion of 3 parts by weight of carbon to one part by weight of hydrogen. If the atomic weight of carbon be 12, the simplest formula for marsh gas, expressing this ratio of C to H, will be CH_4. But the formula C_2H_8 would equally express the ratio $3 : 1 - (12 \times 2 : 1 \times 8)$; this cannot be the formula for marsh gas, however, because the specific gravity (H = 1) of the gas is 8, therefore its molecular weight must be 16 (p. 9), and as the formula is to represent ono molecular weight (p. 9), the formula for marsh gas must be CH_4 $(12 + 4 = 16)$, not C_2H_8 $(24 + 8 = 32)$.

For the purpose of illustration, the analysis of marsh gas may be effected in a Ure's eudiometer (Fig. 37), but a considerable excess of oxygen should be added to moderate the explosion. The eudiometer having been filled with water, 1 c. c. of marsh gas is introduced into it, as described at p. 44, and having been transferred to the closed limb and accurately measured after equalising the level of the water, the open limb is again filled up with water, the eudiometer inverted in the trough, and 12 c. c. of oxygen added; this is also transferred to the closed limb and carefully measured. The electric spark is passed through the mixture (see p. 44), the open limb being closed by the thumb. The level of the water in both limbs is then equalised, and the volume of gas measured. The open limb is filled up with a strong solution of potash, and closed by the thumb, so that the gas may be transferred from the closed to the open limb and back, until its volume is no longer diminished by the absorption of carbon dioxide. The volume of residual oxygen having been measured, the calculation is effected as described above.

The results are more exact when the eudiometer is filled with mercury instead of water, and corrections for temperature and pressure are made.

Fuel.

93. Whilst any combustible substance is applicable for the purpose of producing heat, the forms of fuel actually in use are dependent for their calorific value on the combustion of carbon and hydrogen.* A table showing the composition of the principal fuels will be found on p. 168.

Coal.—The various substances which are classed together under the name of coal are characterised by the presence of carbon as a largely predominant constituent, associated with smaller quantities of hydrogen, oxygen, nitrogen, sulphur, and certain mineral matters which compose the ash. Coal appears to have been formed by a peculiar decomposition or fermentation of buried vegetable matter, resulting in the separation of a large proportion of its hydrogen in the form of marsh-gas (CH_4), and similar compounds, and of its oxygen in the form of carbonic acid gas (CO_2), the carbon accumulating in the residue. Thus, cellulose ($C_6H_{10}O_5$), which constitutes the bulk of woody fibre, might be imagined to decompose according to the equation $2C_6H_{10}O_5 = 5CH_4 + 5CO_2 + C_2$, and the occurrence of marsh gas, and of the paraffin hydrocarbons of similar compositions, as well as of carbonic acid gas, in connexion with deposits of coal, supports this account of its formation. Marsh gas and carbonic acid gas are the ordinary products of the fermentation of vegetable matter, and a spontaneous carbonisation is often witnessed in the "heating" of damp hay. But just as the action of heat upon wood

* The student will meet with a few cases in which the combustion of other elements affords heat for useful purposes, so that such elements are fuels under the particular conditions. For example, the sulphur in pyrites or the aluminium in the mixture known as thermite may be regarded as fuels.

produces a charcoal containing small quantities of the other organic elements, so the carbonising process by which the plants have been transformed into coal has left behind some of the hydrogen, oxygen, and nitrogen; the last, as well probably as a little of the sulphur, having been derived from the vegetable albumin and similar substances which are always present in plants. The chief part of the sulphur is generally present in the form of iron pyrites (FeS_2), derived from some extraneous source. The examination of a peat-bog is very instructive with reference to the formation of coal, as affording examples of vegetable matter in every stage of decomposition, from that in which the organised structure is still clearly visible, to the black carbonaceous mass which only requires consolidation by pressure in order to resemble a true coal. In some cases an important part in the formation of coal may have been played by slow oxidation or decay of the vegetable matter at the expense of atmospheric oxygen held in solution by water; since the hydrogen of the compound would be removed by oxidation taking place at a low temperature, giving rise to a gradual increase in the percentage of carbon.

The three principal varieties of coal—*lignite*, *bituminous coal*, and *anthracite*—present us with the material in different stages of carbonisation; the lignite, or *brown coal*, presenting indications of organised structure, and containing considerable proportions of hydrogen and oxygen, while anthracite often contains little else than carbon and the mineral matter or ash. The following table shows the progressive diminution in the proportions of hydrogen and oxygen in the passage from wood to anthracite.

	Carbon.	Hydrogen.	Oxygen.
Wood	100	12.18	83.07
Peat	100	9.85	55.67
Lignite	100	8.37	42.42
Bituminous coal	100	6.12	21.23
Anthracite	100	2.84	1.74

The combustion of coal is a somewhat complex process, in consequence of the re-arrangement which its elements undergo when the coal is subjected to the action of heat.

As soon as a flame is applied to kindle the coal, the heated portion undergoes destructive distillation, evolving various combustible gases and vapours, which take fire and convey the heat to remoter portions of the coal. Whilst the elements of the exterior portion of coal are undergoing combustion, the heat thus evolved is submitting the interior of the mass to destructive distillation, resulting in the production of various compounds of carbon and hydrogen. Some of these products, such as marsh gas (CH_4) and olefiant gas (C_2H_4), burn without smoke; while others, like benzene (C_6H_6) and naphthalene ($C_{10}H_8$), which contain a very large proportion of carbon, undergo partial combustion, and a considerable quantity of carbon, not meeting with enough heated oxygen in the vicinity to burn it entirely, escapes in a very finely divided state as *smoke* or *soot*, which is deposited in the chimney, mixed with a little ammonium carbonate and small quantities of other products of the distillation of coal. When the gas has been expelled from the coal, there remains a mass of *coke* or cinder, which burns with a steady glow until the whole of its carbon is consumed, and leaves an *ash*, consisting

of the mineral substances present in the coal.* The final results of the perfect combustion of coal would be carbonic acid gas (CO_2), water (H_2O), nitrogen, a little sulphurous acid gas (SO_2), and ash. The production of smoke in a furnace supplied with coal may be prevented by charging the coal in small quantities at a time in front of the fire, so that the highly carbonaceous vapours must come in contact with a large volume of heated air before reaching the chimney. In arrangements for consuming the smoke, hot air is judiciously admitted at the back of the fire, in order to meet and consume the heated carbonaceous particles before they pass into the chimney.

The difference in the composition of the several varieties of coal gives rise to a great difference in their mode of burning.

The table on p. 168 exhibits the composition of representative specimens of the four principal varieties, namely, lignite, bituminous coal, cannel, and anthracite.

The lignites furnish a much larger quantity of gas under the action of heat (and therefore burn with more flame than the other varieties), leaving a coke which retains the form of the original coal; while bituminous coal softens and cakes together—a useful property, since it allows even the dust of such coal to be burnt, if the fire be judiciously managed. Anthracite (*stone coal* or *Welsh coal*) is much less easily combustible than either of the others, and, since it yields but little gas when heated, it usually burns with little flame or smoke. This variety of coal is so compact that it will not usually burn in ordinary grates, but it is much employed for boiler furnaces.

Jet resembles cannel coal in composition.

Accidents occasionally arise from the spontaneous combustion of coal. This appears to be due, in most cases, to the development of heat by the slow combination of some constituents of the coal with atmospheric oxygen, and unless due provision be made for the escape of the heat, its accumulation may raise the temperature to a dangerous degree. The oxidation is more likely to occur if, by careless loading of the coal in the ship, much pulverisation of the fuel has occurred (compare p. 34).

Coke is the residue left by destructively distilling coal, an operation which is conducted in *coke-ovens* when the object is to produce coke for metallurgical use and in retorts when the object is to produce coal gas, the coke being then a by-product. There is no essential difference between the coke-oven and the retort save that the former is considerably the larger of the two, thus distilling a greater weight of coal and producing a denser coke. As all the volatile portions of the coal have been expelled by the distillation, coke burns without flame or smoke, but is correspondingly difficult to ignite.

Wood and Charcoal have already received attention. In this country the use of the former as fuel is limited to its application for kindling less inflammable fuel, like coal. Charcoal is useful in cases where a fuel devoid of sulphur is desirable; it stands in the same relation to wood that coke does to coal as has already been explained (p. 111).

* This ash consists chiefly of silica, alumina and peroxide of iron. When lime is present in the ash, it is liable to fuse into a rough glass or *clinker*, which adheres to the grate bars and causes much inconvenience.

Petroleum finds an increasing application as fuel, particularly the residues from the fractional distillation of the oil (see *Organic Chemistry*) for obtaining illuminating oils. Such residues are known as *astatki*, and when sprayed into a furnace burn with a high heating effect. An advantage of this form of fuel is its freedom from ash.

Gaseous fuel.—The fact that combustible gases can be burnt without the production of smoke and ash renders them a formidable competitor of coal notwithstanding that for an equal heating effect they are more costly. But the more important function of gaseous fuel is as a source of power by its combustion in the cylinder of a gas engine. So far as domestic heating is concerned coal gas is still the sole gaseous fuel used; an air-gas flame (p. 154) is caused to play upon some incombustible and infusible substance like asbestos or fireclay, so that the heat of the flame, which is a feeble radiator, may be converted into the radiant heat of a red-hot solid. The cooling of the flame by contact with the solid necessarily checks the combustion, giving rise to such gases as carbon monoxide and acetylene which are unwholesome to breathe. A flue for carrying away the products of the combustion is therefore essential, but this is less necessary where the gas is allowed to burn with a luminous flame, the radiation from which is considerable while the combustion is practically complete.

94. *Coal gas.*—The manufacture of coal gas is one of the most important applications of the principle of destructive distillation, and affords an excellent example of the tendency of this process to develop new arrangements of the elements of a compound body. The action of heat upon coal, in a vessel from which air is excluded, gives rise to the production of a very large number of compounds containing some two or more of the five elements of the coal, in different proportions, or in different forms of arrangement. Although no clue has yet been obtained to indicate the true arrangement of these elements in the original coal (or, as it is termed, the *constitution* of the coal), it is certain that these various compounds do not exist in it before the application of heat, but are really the results of this application; they are *products*, not *educts*.

The illuminating gas obtained from coal consists essentially of free hydrogen, marsh gas, olefiant gas, and carbonic oxide, with small quantities of acetylene, benzene vapour, and some other substances. Its specific gravity is about 0.4, and is higher the higher the illuminating value of the gas.

A fair general idea of the composition of coal gas is given in the table on p. 168.

The constituents which contribute most largely to the illuminating value of the gas are the vapour of benzene, acetylene, olefiant gas and similar hydrocarbons, represented by C_2H_4 in the table.

The most objectionable constituent is the sulphur present in very small proportion as sulphuretted hydrogen and bisulphide of carbon, for this is converted by combustion into sulphurous and sulphuric acids, which seriously injure pictures, furniture, &c. The object of the manufacturer of coal gas is to remove, as far as possible, everything from it, except the constituents mentioned as essential, and at the same time to obtain as large a volume of gas from a given weight of coal as is consistent with good illuminating value.

The other products of the destructive distillation of coal, the mode of purifying the gas, and the general arrangements for its manufacture, will be described in a later part of the book.

The destructive distillation of coal may be exhibited with the arrangement represented in Fig. 138. The solid and liquid products (tar, ammoniacal liquor, &c.) are condensed in a globular receiver (A). The first bent tube contains, in one limb (B) a piece of red litmus-paper to detect ammonia; and in the other (C) a piece of paper impregnated with lead acetate, which will be blackened by the sulphuretted

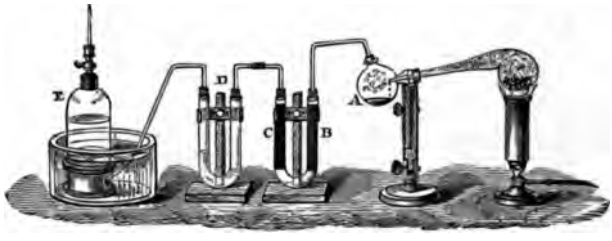


Fig. 138.—Destructive distillation of coal.

hydrogen. The second bent tube (D) contains enough lime-water to fill the bend, which will be rendered milky by the carbonic acid gas. The gas is collected over water in the jar E, which is furnished with a jet from which the gas may be burnt when forced out by depressing the jar in water.

The presence of acetylene in coal gas may be shown by passing the gas from the supply-pipe (A, Fig. 139), first through a bottle (B) containing a little ammonia, then through a bent tube (C) with enough water to fill the bend, and a piece of bright sheet copper immersed in the water in each limb. After a short time the bright red flakes of the copper acetylide will be seen in the water.

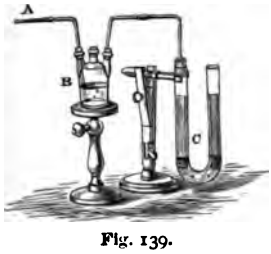


Fig. 139.

So long as coal gas is burnt for producing an illuminating flame and is sold at so much per cubic foot, it is essential that the maker should be compelled to supply it of a standard illuminating value.* This requirement, which entails considerable expense in the manufacture owing to the necessity for "enriching" the gas by adding to it petroleum vapour or some other hydrocarbon that increases the illuminating value, should be changed into a standard heating value now that so much of the gas is used for heating and power purposes, and that the Welsbach system of lighting (which depends solely on the heating value of the gas) is displacing illuminating flames.

Producer gas.—In the manufacture of coal gas some 70 per cent. of the carbon of the coal is left in the retort as coke. It is possible to convert nearly the whole of the carbon of the coal into combustible gas by taking advantage of the fact that CO_2 is reduced to CO by red-hot carbon, $CO_2 + C = 2CO$. The *producer* in which this change is effected, consists of a deep grate into which the fuel is fed from above, the air entering below the charge. The bottom portion of the fuel burns to CO_2, which is reduced to CO † by the hot fuel in the top of the pro-

* In London, 16-candle gas must be supplied; that is, when the gas is burnt from a standard burner at the rate of 5 cubic feet per hour the flame must have an illuminating value equal to that of 16 standard candles.

† See foot-note, p. 132.

ducer; this escapes through a flue to the furnace in which it is to be burnt. Of course, *producer gas* is far from pure CO; it must necessarily contain the nitrogen of the air which supplied the oxygen, and, in addition to this, some CO_2 and the products of the destructive distillation of the coal used, are present.

Water gas.—A gas of more than double the heating effect of producer gas can be obtained from the original fuel by converting it into *water gas*. This process depends on the fact that when steam is passed over heated carbon, a mixture of hydrogen and carbon monoxide is obtained, $C + H_2O = CO + H_2$. Since this reaction is endothermic, the temperature of the carbon must be maintained if the production of the gas is to continue. In practice water gas is made by passing steam into a producer which is already at work, until the temperature has so far fallen that the steam is no longer decomposed. The fuel is then again brought up to the required temperature by a draught of air (producer gas being formed during this stage of the process), and steam is again turned in.

It will be obvious that by blowing an appropriate mixture of steam and air into a producer, a mixture of water gas and producer gas (*semi-water gas*, *Dowson gas*, and *Mond gas*) can be continuously produced.

Calorific value of fuel.—For all practical purposes it may be stated that the amount of heat generated by the combustion of a given weight of fuel depends upon the weights of carbon and hydrogen, respectively, which enter into combination with the oxygen *of the air* when the fuel burns.

It has been ascertained by experiment that 1 gram of carbon (in the form in which it exists in wood-charcoal), when combining with oxygen to form CO_2, produces a quantity of heat which is capable of raising 8080 grams of water from 0° to 1° C. This is usually expressed by saying that the *calorific value of carbon* is 8080, or that carbon produces 8080 *units of heat* during its combustion to CO_2. If the fuel, therefore, consisted of pure carbon, it would merely be necessary to multiply its weight by 8080 to ascertain its calorific value.

One gram of hydrogen, during its conversion into water by combustion evolves enough heat to raise 34,400 lbs. of water from 0° C. to 1° C., so that the *calorific value of hydrogen* is 34,400.

If the fuel consisted of carbon and hydrogen only, its calorific value would be calculated by multiplying the weight of the carbon in 1 lb. of the fuel by 8080, and that of the hydrogen by 34,400, when the sum of the products would represent the *theoretical* calorific value. But if the fuel contains oxygen already combined with it, the calorific value will be diminished, since less oxygen will be required from the air. For example, 1 gram of wood contains 0.5 gram of carbon, 0.06 of hydrogen, and 0.44 of oxygen. Now, oxygen combines with one-eighth of its weight of hydrogen to form water, so that the 0.44 gram of oxygen will convert $0.44 \div 8 = 0.055$ of the hydrogen into water, without evolution of available heat, leaving only 0.005 available for the production of heat. The calorific value of the wood, therefore, would be represented by the sum of 0.005×34400 (= 172) and 0.5×8080 (= 4040) which would amount to 4212; or 1 gram of wood should raise 4212 grams of water from 0° C. to 1° C.

These considerations lead to the following *general formula for calcu-*

lating the calorific value of a fuel containing carbon, hydrogen, and oxygen, where c, h, and o, respectively represent the carbon, hydrogen, and oxygen in 1 gram of fuel.

The calorific value (or number of grams of water which might be heated by the fuel from 0° C. to 1° C) $= 8080\,c + 34400\left(h - \frac{o}{8}\right)$.

The calorific value of a coal, as determined by experiment in a calorimeter is generally higher than that calculated by the above formula.* This arises from lack of knowledge as to how the elements of the coal are combined together.

A convenient form of calorimeter, known as Mahler's bomb, is shown in Fig. 140, and to a smaller scale in position for use in Fig. 141. The weighed substance to be burnt (or the mixture the reaction between the constituents of which is to be started by heat) is placed in a platinum boat C (Fig. 141), attached by metal rods to the cover of the steel bottle B. The cover is screwed on to the bottle, the joint being made tight by means of a lead washer P. The bomb is now connected at N with

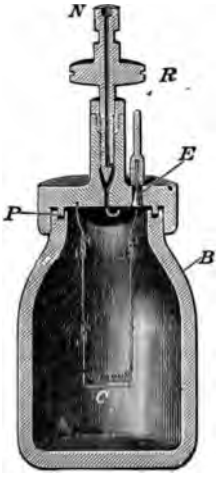


Fig. 140.—Calorimetric bomb.

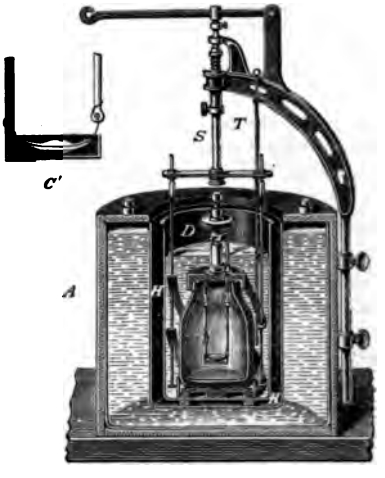


Fig. 141.—Calorimetric bomb.

a tube leading from a bottle of compressed oxygen, and having a pressure gauge inserted in it, and is filled with oxygen under pressure by slowly turning the screw valve R and closing it again when the pressure gauge marks 5–10 atmospheres. The bomb is now placed in the calorimeter chamber D, containing a known weight of water, and surrounded by an air jacket H, itself surrounded by a water jacket A. One of the rods that supports the tray C passes through an insulating plug E in the cover of the bottle B, while the other is in electrical contact with the bottle. Thus, by connecting the end of the insulated wire with one pole of a battery, and the bottle with the other pole, an electric current may be passed through the tray C (or through a platinum spiral embedded in the substance as shown in Fig. 141), so as to heat it to ignite the substance to be burnt. (The quantity of electric current used for this purpose may be measured, and the heat thus introduced into the calorimeter may be calculated from the known equivalency of electric energy and heat energy.) The battery is cut off as soon as ignition has occurred, and the stirrer S having been set in motion the thermometer T is read at intervals, note being taken of the highest point attained and the time occupied in attaining it.

* Results more in accord with the practical value are claimed to be obtained from the following formula, where Q = quantity of heat, C′ = carbon left as coke on distilling the coal, and C″ = carbon contained in the volatile products: $Q = 8080\,C' + 11214\,C'' + 34462\,H$. If much O be present, one-eighth of its weight must be deducted from the H.

If all the heat of the combustion (or reaction) passed into the water of the calorimeter the calculation of the result would be easy; for the weight of the water multiplied by the rise of temperature would represent the heat of combustion. As, however, the whole apparatus shares the heat with the water in the calorimeter chamber, the capacity of the apparatus for heat must be ascertained. This is best effected by burning a known weight of a substance of known calorific value (naphthalene,* for example) in the bomb, and observing how much of the total heat passes into the water in the calorimeter; the difference between this quantity and the known total heat is the amount of heat absorbed by the apparatus, and when divided by the rise of temperature shows the heat capacity of the apparatus.

Suppose that 1 gram of coal has been burnt in the manner described, that the weight of water in the calorimeter is w grams, that the rise of temperature observed is $t°$ C, and that the heat capacity of the apparatus is k gram-units; then the heat of combustion of 1 gram of coal is $wt + kt$. In accurate work a correction must be made for the heat lost by radiation and convection from the calorimeter during the time occupied by the experiment; for the methods of making this correction a text-book on Physics must be consulted.

In the case of compounds of carbon and hydrogen, it has been observed, that even when they have the same composition in 100 parts, they have not of necessity the same calorific value, the latter being affected by the difference in the arrangement of the component atoms of the compound, which causes a difference in the quantity of heat absorbed during its decomposition. Thus, olefiant gas (C_2H_4) and cetylene ($C_{16}H_{32}$) have the same percentage composition, and their calculated calorific values would be identical, but the former is found to produce 11,858 units of heats, and the latter only 11,055.

It must be remembered that the calorific value of a fuel represents the actual amount of heat which a given weight of it is capable of producing, and is quite independent of the manner in which the fuel is burnt. Thus, a hundredweight of coal will produce precisely the same amount of heat in an ordinary grate as in a wind-furnace, though in the former case the fire will scarcely be capable of melting copper, and in the latter it will melt steel. The difference resides in the *temperature* or *calorific intensity* of the two fires: in the wind-furnace, through which a rapid draught of air is maintained by a chimney, a much greater weight of atmospheric oxygen is brought into contact with the fuel in a given time, so that, *in that time*, a greater weight of fuel will be consumed and more heat will be produced: hence the fire will have a higher temperature, for the temperature represents, not the quantity of heat present in a given mass of matter, but the intensity or extent to which that heat is accumulated at any particular point. In the case of the wind-furnace here cited, a further advantage is gained from the circumstance that the rapid draught of air allows a given weight of fuel to be consumed in a smaller space, and, of course, the smaller the area over which a given quantity of heat is distributed, the higher is the temperature within that area (as exemplified in the use of the common burning-glass). In some of the practical applications of fuel, such as heating steam boilers and warming buildings, it is the *calorific value* of the fuel which chiefly concerns us; but the case is different where metals are to be melted, or chemical changes to be brought about by the application of a very high temperature, for it is then the *calorific intensity*, or actual temperature of the burning mass, which has to be considered. No accurate method has yet been devised

* One gram evolves 96,920 gram-units of heat.

for determining by direct experiment the calorific intensity of fuel, nor can this value be ascertained properly by calculation owing to lack of complete data.

It will be instructive, however, to consider how some idea of calorific intensity may be obtained from the calorific value.

Let it be required to calculate the calorific intensity, or actual temperature, of carbon burning in pure oxygen gas.

Twelve grams of carbon combine with 32 grams of oxygen, producing 44 grams of CO_2; hence 1 gram of carbon combines with 2.67 grams of oxygen, producing 3.67 grams of CO_2. It has been seen above that, supposing that the water would bear such an elevation of temperature, and that its specific heat would remain constant, the 1 gram of carbon would raise 1 gram of water from 0° to 8080° C. If the *specific heat* (or heat required to raise 1 gram through 1°) of CO_2 were the same as that of water, 8080° divided by 3.67 would represent the temperature to which the 3.67 grams of CO_2 would be raised, and therefore the temperature to which the solid carbon producing it would be raised in the act of combustion. But the specific heat of carbonic acid gas is only 0.2163, so that a given amount of heat would raise 1 gram of CO_2 to nearly five times as high a temperature as that to which it would raise 1 gram of water.*

Dividing 8080 units of heat (available for raising the temperature of the CO_2) by 0.2163 (the quantity of heat required to raise 1 gram of CO_2 through 1°), we obtain 37355 for the number of degrees through which 1 gram of CO_2 might be raised by the combustion of 1 gram of carbon. But there are 3.67 grams of CO_2 formed in the combustion, so that the above number of degrees must be divided by 3.67 in order to obtain the actual temperature of the CO_2 at the instant of its production, that is, the temperature of the burning mass. The calorific intensity of carbon burning in pure oxygen is therefore (37355° C. ÷ 3.67 =) 10178° C. (or 18352° F.). But if the carbon be burnt in air, the temperature will be far lower, because the nitrogen of the air will absorb a part of the heat, to which it contributes nothing. The 2.67 grams of oxygen required to burn 1 gram of carbon would be mixed, in air, with 8.93 grams of nitrogen, so that the 8080 units of heat would be distributed over 3.67 grams of CO_2 and 8.93 grams of nitrogen. Since the specific heat of CO_2 is 0.2163, the product of 3.67 × 0.2163 (or 0.794) represents the quantity of heat required to raise the 3.67 grams of CO_2 from 0° to 1° C.

The specific heat of nitrogen is 0.2438; hence 8.93 × 0.2438 (or 2.177) represents the quantity of heat required to raise the 8.93 grams of atmospheric nitrogen from 0° to 1° C.

Adding together these products, we find that 0.794 + 2.177 = 2.971 represents the quantity of heat required to raise both the nitrogen and carbonic acid gas from 0° to 1° C.

Dividing the 8080° by 2.971, we obtain 2720° C. (4928° F.) for the number of degrees through which these gases would be raised in the combustion, *i.e.*, for the calorific intensity of carbon burning in air. By heating the air before it enters the furnace (as in the hot-blast iron furnace), of course the calorific intensity would be increased; thus, if the air be introduced into the furnace at a temperature of 600° F., it might be stated, without serious error, that the temperature producible in the furnace would be 5528° F. (4928° + 600°). The temperature might be further increased by diminishing the area of combustion, as by employing very compact fuel and increasing the pressure of the blast.

In calculating the calorific intensity of hydrogen burning in air, from its calorific value, it must be remembered that, in the experimental determination of the latter number, the steam produced in the combustion was condensed to the liquid form, so that its latent heat was added to the number representing the calorific value of the hydrogen; but the latent heat of the steam must be *deducted* in calculating the calorific intensity, because the steam goes off from the burning mass and carries its latent heat with it.

One gram of hydrogen, burning in air, combines with 8 grams of oxygen, producing 9 grams of steam, leaving 26.77 grams of atmospheric nitrogen, and evolving 34400 units of heat.

It has been experimentally determined that the latent heat of steam is 537, that is,

* It is here assumed that the specific heat of gases is constant as the temperature rises; as a fact it increases. The specific heat of steam is calculated to be doubled, and that of CO_2 to be more than doubled, at 1200° C.

1 gram of water, in becoming steam, absorbs 537 units of heat (or as much heat as would raise 537 grams of water from 0° to 1° C.) without rising in temperature as indicated by the thermometer. The 9 grams of water produced by the combustion of 1 gram of hydrogen will absorb, or render latent, $537 \times 9 = 4833$ units of heat. Deducting this quantity from the 34400 units evolved in the combustion of 1 gram of hydrogen, there remain 29567 units of heat available for raising the temperature of the 9 grams of steam and 26.77 grams of atmospheric nitrogen. The specific heat of steam being 0.480 the number $(0.480 \times 9 =) 4.32$ represents the quantity of heat required to raise the 9 grams of steam through 1° C.; and the specific heat of nitrogen (0.2438) multiplied by its weight (26.77 grams) gives 6.53 units of heat required to raise the 26.77 grams of nitrogen through 1° C. By dividing the available heat (29567 units) by the joint quantities required to raise the steam and nitrogen through 1° C. $(4.32 + 6.53 = 10.85)$, we obtain the number 2725° C. (4937° F.) for the calorific intensity of hydrogen burning in air.

The actual calorific intensity of the fuel is not so high as it should be according to theory, because a part of the carbon and hydrogen is converted into gas by destructive distillation of the fuel, and this gas is not actually burnt *in the fire*, so that its calorific intensity is not added to that of the burning solid mass. Again, a portion of the carbon is converted into carbonic oxide (CO), especially if the supply of air be imperfect, and much less heat is produced than if the carbon were converted into carbon dioxide; although it is true that this carbonic oxide may be consumed above the fire by supplying air to it, the heat thus produced does not increase the calorific intensity or temperature of the fire itself.

One gram of carbon furnishes 2.33 grams of carbonic oxide. These 2.33 grams of carbonic oxide evolve, in their combustion, 5599 units of heat. But if the 1 gram of carbon had been converted at once into carbon dioxide, it would have evolved 8080 units of heat, so that $8080 - 5599$, or 2481, represents the heat evolved during the conversion of 1 gram of carbon into carbonic oxide, showing that a considerable loss of heat *in the fire* is caused by an imperfect supply of air. It has been already pointed out that the formation of carbonic oxide is sometimes encouraged with a view to the production of a flame from non-flaming coal, such as anthracite.

The actual calorific intensity of fuel is diminished by the heat consumed in bringing the portion of fuel yet unconsumed, as well as the surrounding parts of the grate, up to the temperature of the fire.

In all ordinary fires and furnaces, a large amount of heat is wasted in the current of heated products of combustion escaping from the chimney. Of course, a portion of this heat is necessary in order to produce the draught of the chimney. In boiler furnaces it is found that, for this purpose, the temperature of the air escaping from the chimney must not be lower than from 500° to 600° F. If the fuel could be consumed by supplying only so much air as contains the requisite quantity of oxygen, a great saving might be effected, but in practice about twice the calculated quantity of air must be supplied in order to effect the removal of the products of combustion with sufficient rapidity.

Much economy of fuel results from the use of furnaces constructed on the principle of Siemens' *regenerative furnace*, in which the waste heat of the products of combustion is absorbed by a quantity of firebricks, and employed to heat the air before it enters the furnace, two chambers of firebricks doing duty alternately, for absorbing the heat from the issuing gas, and for imparting heat to the entering air, the current being reversed by a valve as soon as the firebricks are strongly heated. This system is best adapted for the use of gaseous fuel which

can also be heated by the hot fire bricks before its combustion, a very high temperature being thus attainable.

The following table shows the percentage composition of samples of the principal varieties of fuel together with their calorific values:—

	C.	H.	O.	N.	S.	Ash.	Calorific Value.
Wood (oak)	50.18	6.08	42.64	0.10	—	1.00	3,000
Peat	54.38	5.08	29.54	1.31	—	8.69	4,000
Lignite	66.32	5.63	22.86	0.56	2.36	2.27	5,000
Bituminous coal	78.57	5.29	12.88	1.84	0.39	1.03	8,250
Wigan cannel	80.06	5.53	8.09	2.12	1.50	2.70	8,750
Charcoal	81.97	2.30	14.15	—	—	1.60	8,000
Anthracite	90.39	3.28	2.98	0.83	0.91	1.61	9,000
Coke	92.48	0.47	0.93	0.73	1.14	4.27	8,000
Petroleum	85.00	13.00	2.00	—	—	—	11,000

	H.	CH_4	CO	C_2H_4*	CO_2	N.	O.	Calorific Value.†
Coal gas (Newcastle coal)	43.99	39.36	6.42	4.12	—	5.40	0.40	170,000
„ cannel	41.72	41.88	4.98	8.72	—	2.71	—	
Producer gas	2.20	7.40	22.80	—	3.60	63.50	0.50	28,000
Water gas	48.00	—	41.00	—	6.00	5.00	—	74,000
Mond gas	29.00	2.00	11.00	—	16.00	42.00	—	40,000

Types of Chemical Compounds.

95. It has been seen in the preceding pages that—

One vol. chlorine combines with one vol. hydrogen.
One „ oxygen „ „ two vols. „
One „ nitrogen „ „ three „ „
One „ carbon „ „ four „ „

and that although other compounds of these elements with hydrogen may exist they are less stable than the compounds in question and contain, moreover, a smaller proportion of hydrogen.

The composition of the four compounds in question may be represented by the formulæ ClH, OH_2, NH_3 and CH_4 respectively, and if the valency of an element be defined as the maximum number of atoms of hydrogen with which one atom of the element can combine, chlorine, oxygen, nitrogen, and carbon are respectively mono- di- tri- and tetravalent elements. It will be found that no atom can combine with more than four atoms of hydrogen. This being the case, the hydrogen compounds of all elements must fall in one or other of the four classes of which hydrochloric acid, water, ammonia, and marsh gas are the *types*.

One of the atoms of H in each of these typical molecules may be exchanged for another atom, usually a metal; thus ClH gives ClNa, OH_2 gives OHNa, NH_3 gives NH_2Na, CH_4 gives CH_3Na. It is evident that the groups OH, NH_2, and CH_3 are on the same footing as the elementary atom Cl in ClH; as already explained, each is a *radicle*—that is, *a group capable of being exchanged for an element*. Since

* Including benzene vapour, acetylene, etc.
† Gram units per cubic foot (28.315 litres).

each of these radicles is equivalent to Cl, which unites with one atom of H, and is therefore monovalent, each is a monovalent radicle.

The elements may be roughly divided into those which form stable compounds with hydrogen and those which are substituted for hydrogen ; the latter class is approximately coincident with that which includes the elements forming basic oxides (*i.e.*, the metals), whilst the former class contains those elements which form acid oxides or anhydrides (*i.e.*, the non-metals). The valency of a non-metal is thus fixed by the number of atoms of hydrogen in a molecule of its maximum hydrogen compound, whilst that of a metal is determined by the formula for its compound with Cl or with O.

Thus, sulphur, whose maximum hydrogen compound is SH_2, falls under the oxygen type, and is divalent towards hydrogen ; phosphorus, of which PH_3 is the hydrogen compound containing the largest proportion of hydrogen, falls under the nitrogen type, and is trivalent.

Again, the analysis of zinc oxide shows that the proportion of zinc to oxygen in this compound is represented by the formula OZn ; zinc oxide, therefore, is of the type OH_2, one atom of the metal having been substituted for H_2. Thus, Zn falls under the oxygen type, and is divalent, from which fact it would be possible to foretell the composition of its chloride ; for, since this can only be formed by the substitution of two atoms of H, the type ClH must be doubled, Cl_2H_2, before the zinc chloride can be formed ; the formula in question would then be Cl_2Zn.

The analysis of the higher chloride of iron (two are known) shows that the formula for this chloride is $FeCl_3$, showing that the iron has displaced the H in the type ClH trebled, or Cl_3H_3. From this fact the formula for the higher oxide of iron would be prophesied to be O_3Fe_2 ; for, since Fe displaces H_3, the type OH_2 must be trebled. O_3H_6, in order that the H may be totally displaced by the iron, two atoms of which will displace six of H.

It has been already noted that the valency of nitrogen towards H is not the limit of the atom-fixing power of this element. It will be noted in the sequel that the atom-fixing power which an element exhibits towards oxygen is generally greater than that exhibited towards hydrogen.

CHLORINE.

Cl = 35.5 parts by weight = 1 volume.

96. This element is never found in the uncombined state, but is very abundant in the mineral world in the forms of sodium chloride (common salt) and potassium chloride. In these forms also it is an important constituent of the fluids of the animal body, but as it is not found in sufficient proportion in vegetable food, or in the solid parts of animal food, a quantity of salt must be added to these in order to form a wholesome diet. Sodium chloride is indispensable as a raw material for several of the most useful arts, such as the manufacture of soaps and glass, bleaching, &c. ; in fact, it is the source of three of the most generally useful chemical products—viz., chlorine, hydrochloric acid, and soda.

About the middle of the seventeenth century, a German chemist named Glauber distilled some common salt with sulphuric acid, and obtained a strongly acid liquid to which he gave the name *muriatic acid* (from *muria*, brine); this was proved to be identical with the acid long known to the alchemist as *spirit of salt* (obtained by distilling salt with clay). The saline mass which was left after the experiment was then termed Glauber's salt, but afterwards received its present name of sodium sulphate.

It was undoubtedly a natural inference from this experiment that common salt was composed of muriatic acid and soda, and that the sulphuric acid had a greater attraction for the soda than the muriatic acid had, which was therefore displaced by it. In accordance with this

view, common salt was called muriate of soda, without further question, until the year 1810, when the experiments of Davy proved that it was really composed of the two elementary substances, chlorine and sodium, and must therefore be styled, as it now is, sodium chloride, and represented by the formula NaCl. It was further shown by Davy that the muriatic acid was really composed of chlorine and hydrogen, and that it was, in fact, HCl, or chloride of sodium (NaCl), in which the sodium had been displaced by hydrogen.

Preparation of chlorine.—In order to extract chlorine from common salt, the salt is heated with black oxide of manganese and diluted sulphuric acid, when the sulphates of sodium and manganese are left in solution, and chlorine escapes in the form of gas—

$$2NaCl + MnO_2 + 2H_2SO_4 = Na_2SO_4 + MnSO_4 + 2H_2O + Cl_2.$$

40 grms. of common salt may be mixed with 30 grms. of binoxide of manganese, introduced into a retort (Fig. 142) and a cold mixture of 44 c.c. of

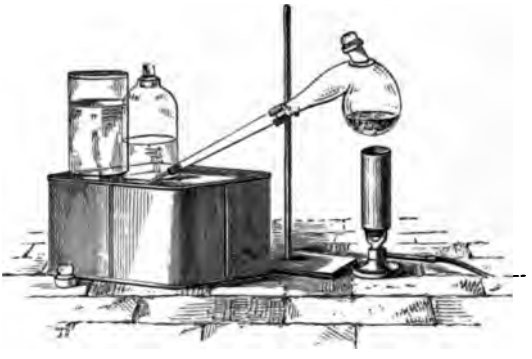


Fig. 142.—Preparation of chlorine.

strong sulphuric acid with 110 c.c. of water poured upon it. The retort having been well shaken, to wet the powder thoroughly with the acid, a very gentle heat is applied, and the gas collected in bottles filled with water and inverted in the pneumatic trough; the stoppers, previously greased, are then inserted under water into the bottles. The first bottle or two contains the air from the retort, and therefore has a paler colour than the pure chlorine afterwards collected. It is advisable to keep a jar filled with water standing ready on the shelf of the trough, so that any excess of chlorine may be passed into it instead of being allowed to escape into the air and cause serious inconvenience. The bottles of moist chlorine must always be preserved in the dark. Chlorine may also conveniently be prepared by gently heating 30 grms. of binoxide of manganese with 110 c.c. of common hydrochloric acid; $MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2$. Either of the above methods will furnish about 2800 c.c. of chlorine. If chlorine be required free from HCl, it may be passed through a strong solution of copper sulphate—

$$CuSO_4 + 2HCl = CuCl_2 + H_2SO_4.$$

On a large scale chlorine is made by heating manganese dioxide with hydrochloric acid in stills built up of sandstone slabs.

In Weldon's manganese recovery process for the manufacture of chlorine, the manganese is made to act as a carrier of oxygen from the atmosphere to the hydrogen of the HCl, setting the Cl free. For this purpose the chloride of manganese obtained in the above process is decomposed by lime; $MnCl_2 + CaO = CaCl_2 + MnO$. By mixing the MnO with more lime, and blowing air through the mixture MnO_2 is reproduced, and may be employed for decomposing a fresh quantity of HCl. In *Deacon's process*, a mixture of air and hydrochloric acid gas is passed over hot fire-

brick which has been soaked in solution of copper sulphate and sodium sulphate, and dried. The final result is expressed by the equation $2HCl + (N_4 + O) = H_2O + Cl_2 + N_4$, so that the chlorine obtained is mixed with twice its volume of nitrogen, which does not interfere seriously with its useful application. The action of the copper-salt has not been clearly explained, but it appears to depend upon the instability of the chlorides of copper under the influence of heat and oxygen.

Chlorine is now made by electrolysing NaCl, a process which, among others, will receive notice under *Alkali*.

Properties of chlorine.—The physical and chemical properties of chlorine are more striking than those of any element hitherto considered. Its colour, whence it derives its name (χλωρός, pale green), is bright greenish-yellow, its odour insupportable. It is twice and a half as heavy as air (sp. gr. 2.47), and may be reduced to the liquid state by cooling it to $-34°$ C. (its boiling-point), or by a pressure of 8.5 atmospheres at 12.5° C. If a bottle of chlorine be held mouth downwards in water, its stopper removed, one-third of the chlorine decanted into a jar, and the rest of the gas shaken with the water in the bottle, the mouth of which is closed by the palm of the hand, the water will absorb about twice its volume of chlorine, producing a partial vacuum in the bottle, which will be held firmly against the hand by atmospheric pressure. If air be then allowed to enter, and the bottle again shaken so long as there is any absorption, a saturated solution of chlorine (*liquor chlori*, *chlorine water*) will be obtained. By exposing this yellow solution to a temperature approaching 0° C., yellow crystals of *chlorine hydrate* ($Cl.4H_2O$) are obtained, the liquid becoming colourless; under atmospheric pressure the crystals decompose into water and chlorine at 9.6° C.

When the water in the pneumatic trough, over which chlorine is being collected, happens to be very cold, the gas is often so foggy as to be quite opaque, in consequence of the deposition of minute crystals of the hydrate. On standing, the gas becomes clear, crystals of the hydrate being deposited like hoar-frost upon the sides of the bottle; the gas also becomes clear when the bottles are slightly warmed.

Chlorine hydrate affords a convenient source of liquid chlorine. The crystals are rammed into a pretty strong tube closed at one end, about 12 inches long, and ½ an inch in diameter, previously cooled in ice. The tube, having been nearly filled with the crystals, is kept surrounded with ice, whilst its upper end is gradually softened in the blowpipe flame and drawn off so as to be strongly sealed. When this tube is immersed in water at 38° C., the chlorine separates from the water, and two layers of liquid are formed, the lower one consisting of amber yellow liquid chlorine (sp. gr. 1.33), and the upper of a pale yellow aqueous solution of chlorine. On allowing the tube to cool again, the crystalline hydrate is reproduced, even at common temperatures, being more permanent under pressure. It may even be sublimed in a sealed tube.

Liquid chlorine is now an article of commerce, being transported in steel bottles.

The critical temperature of chlorine is 146° C., and its critical pressure 93.5 atm.

The most characteristic chemical feature of chlorine is its powerful attraction for many other elements at the ordinary temperature. Among the non-metals, hydrogen, bromine, iodine, sulphur, selenium, phosphorus, and arsenic combine spontaneously with chlorine, and nearly all the metals behave in the same way.*

* The presence of moisture appears to be as essential for the combination of chlorine with other elements as it is for the combination of oxygen with other elements. Thus sodium may be fused in *absolutely dry* chlorine gas without alteration, while in ordinary chlorine violent combustion occurs. When the sodium is heated to redness in the dry gas it burns explosively.

A piece of dry phosphorus in a deflagrating spoon, immersed in a bottle of chlorine (Fig. 143), takes fire spontaneously, combining with the chlorine to form phosphorous chloride (PCl_3). A tall glass shade may be placed over the bottle, which should stand in a plate containing water, so that the fumes may not escape into the air. If phosphorus be placed in a bottle of oxygen, to which a small quantity of chlorine has been added, it will burst out after a minute or two into most brilliant combustion.

Powdered antimony (the metal, not the sulphide), sprinkled into a bottle of chlorine (Fig. 144), descends in a brilliant shower of white sparks, the antimony burning in the chlorine to form antimonious chloride ($SbCl_3$). A little water should be placed at the bottom of the bottle to prevent it from being cracked.

If a flask, provided with a stop-cock (Fig. 145), be filled with leaves of *Dutch metal* (an alloy of copper and zinc resembling gold-leaf), exhausted of air, and screwed on to a capped jar of chlorine standing over water, on opening the stop-

Fig. 143.

Fig. 144.

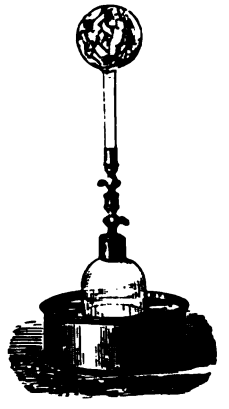


Fig. 145.

cocks so that the chlorine may enter the flask, the metal burns with a red light, forming thick yellow fumes containing cupric chloride ($CuCl_2$), and zinc chloride ($ZnCl_2$). A gold leaf suspended in chlorine is not immediately attacked, but gradually becomes auric chloride ($AuCl_3$).

97. The most important useful applications of chlorine depend upon its powerful chemical attraction for hydrogen. The two gases may be mixed without combining, if kept in the dark; but when the mixture is exposed to light, they combine to form hydrogen chloride (HCl) with a rapidity proportionate to the intensity of the *actinic* rays (or rays capable of inducing chemical change) in the light employed. Exposed to gas-light or ordinary diffused daylight, the H and Cl combine slowly; but direct sunlight causes sudden combination, attended with explosion, resulting from the expansion which the hydrogen chloride formed suffers by the heat evolved in the act of combination (22,000 gram units per 36.5 grams of HCl formed). The light of magnesium burning in air, and some other artificial lights, also cause sudden combination. The gases also combine at about 300° C., and explode on application of a lighted taper.

Two pint gas-bottles should be ground so that their mouths may be fitted accurately to each other, and filled respectively with dry hydrogen and dry chlorine, both gases having been dried by passing through oil of vitriol, and collected, the hydrogen by upward, and the chlorine by downward, displacement of air. The mouths should be slightly greased before the bottles are filled with gas, and after-

wards closed with glass plates. On placing the bottles together, and removing the plates so that the gases may come in contact (see Fig. 69), the yellow colour of the chlorine will be permanent so long as the mixture is kept in the dark, but on exposure to daylight the colour will gradually disappear, the hydrochloric acid gas being colourless. If the bottles be now closed with glass plates, the small quantity of gas which escapes during the operation will be seen to fume strongly in air, a property not possessed either by hydrogen or chlorine; and when the necks of the bottles are immersed in water, and the glass plates withdrawn, the water will gradually absorb the gas, and be forced into the bottles so as to fill them, with the exception of a small space occupied by the air accidentally admitted, showing that the hydrochloric acid gas possesses the joint volumes of the hydrogen and chlorine. If the water be tinged with blue litmus, it will be strongly reddened as it enters the bottles.

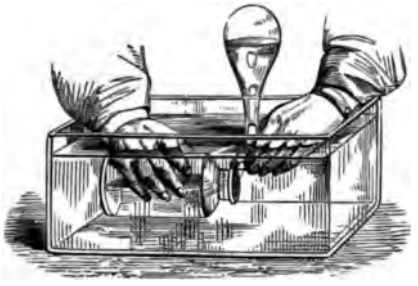


Fig. 146.

The sudden union of the gases with explosion may be safely exhibited in a Florence flask. The flask is filled with water, which is then poured out into a measure. Exactly half the water is returned to the flask, and its level in the latter carefully marked with a diamond or file. The flask, having been again filled with water, is closed with the thumb and inverted in the pneumatic trough, so that hydrogen may be passed up into it to displace one-half of the water. A short-necked funnel is then inserted, under the water, into the neck of the flask, and chlorine rapidly decanted up from a gas-bottle (Fig. 146) until the rest of the water has been displaced. The flask is now raised from the water and quickly closed with a cork (Fig. 147), through which pass two gutta-percha-covered copper wires, the ends of which have been stripped and brought sufficiently near to each other to allow of the passage of the electric spark within the flask. The ends external to the flask are also stripped and bent into hooks, for convenient connection with the conducting wires. The flask is placed upon the ground, and covered with a wooden box to prevent the pieces from flying about. On connecting the copper wires with the conducting wires from an induction coil or an electrical machine, it will be heard, on passing the spark, that the mixture has violently exploded; on raising the box, it will be found filled with strong fumes of hydrochloric acid, and a heap of small fragments of glass will represent the flask.

Fig. 147.

A flask filled in the same way with the mixture of hydrogen and chlorine may be attached to the end of a long stick, and thrust out into the sunlight, when it explodes with great violence. To illustrate the direct combination of H and Cl under the influence of artificial light, a strong half-pint gas cylinder is half filled with H, over water, then filled up quickly with Cl, also over water, closed with a thin plate of mica, placed mouth upwards on the table, and a piece of burning magnesium tape held close to the side of the cylinder; the lightness of the mica plate obviates any danger.

A mixture of H and Cl which is to be exploded by light must consist of exactly equal volumes, for a slight excess of either gas greatly diminishes the sensitiveness of the mixture to light; thus a mixture of 100 vols. of Cl. with 100.6 vols. H is 38 per cent. less sensitive than a mixture of equal volumes.

The attraction of chlorine for hydrogen enables it to decompose water. Chlorine-water may be preserved in the dark without change;

but when exposed to light, it loses the smell of chlorine and becomes converted into weak hydrochloric acid, the oxygen being liberated; $H_2O + Cl_2 = 2HCl + O$.* The decomposition is much more rapid at a red heat, so that oxygen is obtained in abundance by passing a mixture of chlorine and steam through a red-hot tube.

For this experiment a porcelain tube is used, loosely filled with fragments of broken porcelain, to expose a large heated surface. This tube is gradually heated to redness in a gas furnace (Fig. 148). One end of it receives the mixture of chlorine with steam, obtained by passing the chlorine evolved from hydrochloric acid and

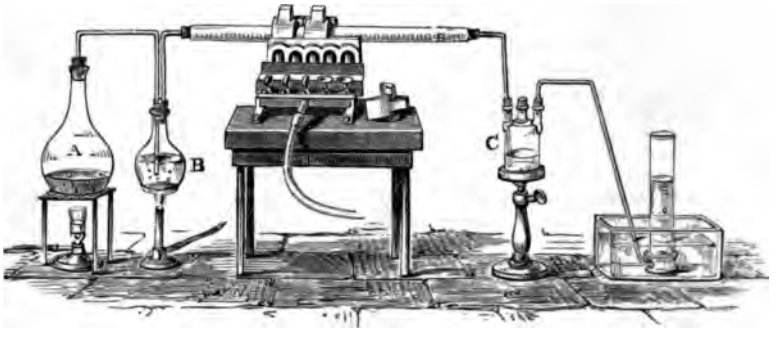


Fig. 148.—Steam decomposed by chlorine.

manganese dioxide in A, through a flask (B) of boiling water. The other end of the tube is connected with a bottle (C) containing solution of potash, to absorb any excess of chlorine and the hydrochloric acid formed; from this bottle the oxygen is collected over the pneumatic trough.

The combination of hydrogen with chlorine may obviously be regarded as the substitution of an atom of chlorine for an atom of hydrogen in a molecule of hydrogen, $HH + ClCl = HCl + HCl$, the atom of hydrogen substituted having been removed as HCl. Thus viewed it becomes typical of a large number of cases in which two atoms of chlorine react with a hydrogen compound, one of them bearing away a hydrogen atom in the form of HCl whilst the other takes the place of the hydrogen thus removed. Such a substitution of chlorine for hydrogen is known as *metalepsis*, and is a very common reaction of chlorine with hydrocarbons; since the formation of hydrogen chloride is initiated by light it is not surprising that metalepsis is aided by this agency.

When equal volumes of marsh gas (CH_4) and chlorine are mixed and exposed to sunlight the volume of the mixture remains unaltered, but after a time the yellow colour of the chlorine is no longer observed, and the gas is found to consist of equal volumes of methyl chloride and hydrogen chloride, $CH_4 + Cl_2 = CH_3Cl + HCl$. The metalepsis may be carried further by mixing methyl chloride with more chlorine, $CH_3Cl + Cl_2 = CH_2Cl_2 + HCl$. Again CH_2Cl_2 with Cl_2 will yield *chloroform* $CHCl_3$, and this with Cl_2 will yield *carbon tetrachloride* CCl_4. By mixing one volume of marsh gas with its own volume of CO_2, to prevent violent action, and adding four volumes of chlorine, an oily mixture, containing chiefly $CHCl_3$ and CCl_4 is formed under the influence of daylight.

Since water is decomposed by chlorine, it is not surprising that most

* A portion of this oxygen becomes hypochlorous acid (HClO), chloric acid ($HClO_3$) and perchloric acid ($HClO_4$), particularly if the light be not very intense.

other hydrogen compounds are attacked by it. Ammonia (NH_3) is acted on with great violence. If a stream of ammonia gas issuing from a tube connected with a flask in which solution of ammonia is heated be passed into a bottle of chlorine, it takes fire immediately, buring with a peculiar flame, and yielding thick white clouds of ammonium chloride; $4NH_3 + Cl_3 = 3NH_4Cl + N$. A piece of folded filter-paper dipped in strong ammonia, and immersed in a bottle of chlorine, will exhibit the same effect. When the chlorine is allowed to act upon ammonium chloride, its operation is less violent, and one of the most explosive substances, *nitrogen chloride*, NCl_3, is produced.

Many of the compounds of hydrogen with carbon are also decomposed with violence by chlorine. When a piece of folded filter-paper is dipped into oil of turpentine ($C_{10}H_{16}$), and afterwards into a bottle of chlorine, it bursts into a red flame, liberating voluminous clouds of carbon and hydrochloric acid. Acetylene (C_2H_2) was found to explode spontaneously with chlorine when exposed to light (page 141). The striking decomposition of olefiant gas (C_2H_4) by chlorine on the approach of a flame has already been noticed (page 143). When a lighted taper is immersed in pure chlorine, it is extinguished; but if a little air be present, it continues to burn with a small red flame, the hydrogen only of the wax combining with the chlorine, whilst the carbon separates in black smoke, mixed with the hydrochloric fumes. A mixture of chlorine with an equal volume of oxygen burns up much of the carbon, with a very pretty effect. When chlorine is brought in contact with the flame of a spirit-lamp, it renders the flame luminous by causing the separation of solid particles of carbon (page 149). It has been seen, in the case of olefiant gas, that chlorine sometimes combines directly with the hydrocarbons.

The attraction of chlorine for hydrogen enables the moist gas to act as an oxidising agent. Thus, if marsh gas and chlorine be mixed in the presence of water, and exposed to daylight, the water is decomposed, its hydrogen combining with the chlorine, and its oxygen with the carbon of the marsh gas; $CH_4 + 2H_2O + Cl_8 = CO_2 + 8HCl$.

98. The powerful bleaching effect of chlorine upon organic colouring matters is now easily understood. If a solution of chlorine in water be poured into solution of indigo (*sulphindigotic acid*), the blue colour of the indigo is discharged, and gives place to a comparatively light yellow colour. The presence of water is essential to the bleaching of indigo by chlorine, the dry gas not affecting the colour of dry indigo. The indigo is first oxidised at the expense of the water and converted into *isatin*, which is then acted upon by the chlorine and converted by metalepsis into *chlorisatin*, having a brownish-yellow colour—

$$C_{16}H_{10}N_2O_2\ (\textit{Indigo}) + 2H_2O + Cl_4 = 2C_8H_5NO_2\ (\textit{Isatin}) + 4HCl$$
$$C_8H_5NO_2\ (\textit{Isatin}) + Cl_2 = C_8H_4ClNO_2\ (\textit{Chlorisatin}) + HCl.$$

Nearly all vegetable and animal colouring matters contain carbon, hydrogen, nitrogen, and oxygen, and are converted by moist chlorine into products of oxidation or chlorination which happen to be colourless, or nearly so.

It might be thought that, since water is decomposed by chlorine only in light, chlorine would not behave as an oxidising agent in the dark. Bleaching by chlorine can, however, proceed in the absence of light because the colouring matter, being ready to combine with oxygen, exerts

attraction on the oxygen of the water, sufficiently powerful to weaken the union between the H and O so that the chlorine can effect the decomposition.

That dry chlorine will not bleach may be shown by shaking some oil of vitriol in a bottle of the gas and allowing it to stand for an hour or two, so that the acid may remove the whole of the moisture. A piece of crimson paper dried at a moderate heat and suspended in the bottle while warm, remains unbleached for hours; but a similar piece suspended in a bottle of moist chlorine is bleached almost immediately. If characters be written on crimson paper with a wet brush, and the paper placed in a jar beside a bottle of chlorine (Fig. 149), it will be found on removing the stopper that white characters soon make their appearance on the red ground.

Fig. 149.

When a collection of coloured linen or cotton fabrics, or of artificial flowers, is exposed to the action of moist chlorine or of chlorine-water, those which are dyed with organic colouring matters are bleached at once, whilst the mineral colours for the most part remain unaltered. Green leaves immersed in chlorine acquire a rich autumnal brown tint, and are eventually bleached. All flowers are very readily bleached by the gas.

Chlorine is very extensively employed for bleaching linen and cotton, the gas acting upon the colouring matter without affecting the fibre; but silk and wool present much less resistance to chemical action, and would be much injured by chlorine so that they are always bleached by sulphurous acid gas.

Neither chlorine itself nor its solution in water can be very conveniently used for bleaching on the large scale, on account of the irritating effect of the gas, so that it is usual to employ it in the form of *chloride of lime*, from which it can be easily liberated as it is wanted.

99. The explanation above given of the bleaching effect of chlorine may probably be applied also to its so-called *disinfecting* properties. The atmosphere, in particular localities, is occasionally contaminated with micro-organisms, some of which are known only by their injurious effects upon the health, their quantity being so small that they do not appear in the results of the analysis of such air. Since, however, these minute forms of life appear to be killed by the same agents which are usually found to decompose organic compounds, chlorine has been very commonly employed to combat these insidious enemies to health.

Among the offensive and unhealthy products of putrefaction of animal and vegetable matter, sulphuretted hydrogen, ammonia, and like bodies are found. That chlorine breaks up these hydrogen compounds is well known; hence its great value for removing the unwholesome properties of the air in badly drained houses, &c.

100. The discovery of chlorine, and the discussions which ensued with respect to its real nature, contributed very largely to the advancement of chemical science. About the year 1770, the Swedish chemist Scheele (who afterwards discovered oxygen) first obtained chlorine by heating manganese ore with muriatic acid.

The construction which Scheele put upon the result of this experiment was one which was consistent with the chemistry of that date. He supposed the muriatic acid to have been deprived of *phlogiston*, and hence chlorine was termed by him *dephlogisticated muriatic acid*. This phlogiston had long been a subject of contention among philosophers, having

been originally assumed to exist in combination with all combustible bodies, and to be separated from them during their combustion. Towards the decline of the phlogistic theory, attempts were made to prove the identity of this imaginary substance with hydrogen, which shows how very nearly Scheele's reasoning approached to the truth, even with the very imperfect light which he then possessed. Berthollet's movement was retrograde, when, ten years afterwards, he styled chlorine *oxygenised muriatic* or *oxymuriatic acid*; but the experiments of Gay-Lussac and Thénard, and more particularly those of Davy in 1811, proved decisively that hydrochloric acid was composed of chlorine and hydrogen, and that the effect of the black oxide of manganese in Scheele's experiment was to remove the hydrogen in the form of water, thus setting the chlorine at liberty.

Hydrochloric Acid, or Hydrogen Chloride.

HCl = 36.5 parts by weight = 2 vols.

101. This acid is found in nature among the gases emanating from active volcanoes, and occasionally in the spring and river waters of volcanic districts. For use it is always prepared artificially by the action of sulphuric acid upon common salt—

$$\underset{\text{Common salt.}}{NaCl} + H_2SO_4 = HCl + \underset{\text{Hydrogen-sodium sulphate.}}{NaHSO_4}$$

—the sodium of the common salt changing places with the hydrogen of the sulphuric acid.

20 grams of common salt (previously dried in an oven) are introduced into a dry flask (Fig. 150), to which has been fitted, by means of a perforated cork, a tube bent twice at right angles, to allow the gas to be collected by downward displacement. 30 c.c. of strong H_2SO_4 are poured upon the salt, and, the cork having been inserted, the flask is very gently heated, in order to promote the disengagement of the hydrochloric acid gas, which is collected in a perfectly dry bottle, the mouth whereof when full, may be covered with a glass plate smeared with a little grease. While being filled, the bottle may be closed with a perforated card.

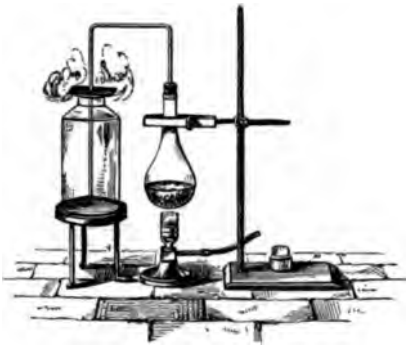


Fig. 150.—Preparation of hydrochloric acid gas.

At a red heat the whole of the hydrogen in the H_2SO_4 can be converted into HCl. $2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl$; but this is never effected in practice.

Common salt in powder sometimes froths to a very inconvenient extent with sulphuric acid; it is therefore often preferable to employ fragments of rock salt or of fused salt, prepared by fusing the common salt in a clay crucible, and pouring it on to a clean dry stone.

Hydrogen chloride is also conveniently prepared by dropping strong H_2SO_4 from a funnel provided with a stopcock into commercial strong hydrochloric acid. The apparatus may take the form shown in Fig. 156, the U-tube being omitted.

The bottle will be known to be filled with gas by the abundant escape of the dense fumes which hydrogen chloride, itself transparent, produces by condensing the moisture of the air; for since the gas is heavier than air (sp. gr. 1.278), it will not escape in any quantity from the

bottle until the latter is full. The odour of the gas is very suffocating, but not nearly so irritating as that of chlorine. The powerful attraction for water is one of the most important properties of this gas.

If a jar of hydrogen chloride be closed with a glass plate and inverted under water, it will be found on removing the plate that the gas is absorbed with great rapidity, the water being forced up into the bottle by the pressure of the external air, in proportion as the gas is absorbed. The experiment may also be made as in the case of ammonia (Fig. 69, see page 84).

The dissolution of 36.5 grams HCl in excess of water evolves 17,200 calories.

The liquid hydrochloric, or *muriatic acid* of commerce, is a solution of the gas in water, and may be recognised by the grey fumes, with the peculiar odour of the acid, which it evolves when exposed to the air. One pint of water at a temperature of 5° C. is capable of absorbing 480 pints of hydrochloric acid gas, forming $1\frac{1}{3}$ pints of the solution, having the specific gravity 1.21. The strength of the acid purchased in commerce is usually inferred from the specific gravity, by reference to tables indicating the weight of HCl contained in solutions of different specific gravities. The strongest hydrochloric acid (sp. gr. 1.21) contains 43 per cent., by weight of the gas. At − 18° C. it deposits crystals of HCl.2Aq. The common acid has usually a bright yellow colour, due to the accidental presence of a little ferric chloride (Fe_2Cl_6).

This acid is produced in enormous quantities in the alkali works, where common salt is decomposed by sulphuric acid in order to convert it into sodium sulphate, as a preliminary step to the production of sodium carbonate. The alkali manufacturer is compelled to condense the gas, for it is found to wither up the vegetation in the neighbourhood. For this purpose the hydrochloric acid gas is drawn up from the furnace through vertical cylinders filled with coke, over which streams of water are made to trickle. The water absorbs the acid, and is drawn off from below (see *Alkali*).

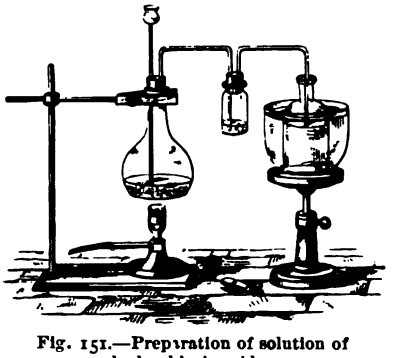


Fig. 151.—Preparation of solution of hydrochloric acid.

In preparing a pure solution of the acid for chemical use on a small scale, the gas prepared as above may be passed into a small bottle containing a very little water, to wash the gas, or remove any sodium sulphate which may splash over, and then into a bottle about two-thirds filled with distilled water, the tube delivering the gas passing only about $\frac{1}{16}$ inch below the surface, so that the heavy solution of hydrochloric acid may fall to the bottom, and fresh water may be presented to the gas (Fig. 151).

Pure solution of hydrochloric acid is sometimes prepared on a large scale by allowing concentrated sulphuric acid to run into the common hydrochloric acid, when the gas is evolved, and is washed and passed into water.

When the concentrated solution of hydrochloric acid is heated in a retort it evolves abundance of hydrochloric acid gas, rendering it probable that it is not a true chemical compound of water with the acid. The evolution of gas ceases when the remaining liquid contains 20 per

cent. of acid (and has a sp. gr. of 1.10). If a weaker acid than this be heated, it loses water until it has attained this strength, when it distils unchanged at 110° C.*

The concentrated solution forms a very convenient source from which to procure the gas. It may be heated in a flask, and the gas dried by passing through a bottle filled with fragments of pumice-stone wetted with concentrated sulphuric acid, being collected over the mercurial trough (Fig. 152).

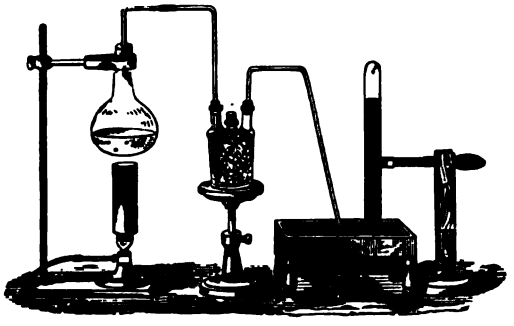


Fig. 152.

The avidity with which water absorbs hydrogen chloride is the more remarkable, because this gas can be liquefied only under a very high pressure, amounting at the ordinary temperature to about 40 atmospheres. The liquid boils at −80° C. and solidifies at a lower temperature, melting at −112° C. The sp. gr. of the liquid is 0.91 at 0° C. The critical temperature of the gas is 52° C. and the critical pressure is 86 atmospheres.

The liquefied hydrogen chloride has comparatively little action even upon those metals which decompose its aqueous solution with great violence; quicklime is unaffected by it, and solid litmus dissolves in it with a faint purple colour, instead of the bright red imparted by the aqueous hydrochloric acid. Dry hydrochloric acid gas is not absorbed by calcium carbonate.†

The injurious action of hydrochloric acid gas upon growing plants is probably connected with its attraction for water. If a spray of fresh leaves is placed in a bottle of hydrochloric acid, it becomes at once brown and shrivelled. One part of HCl in 25,000 of air is fatal to plants.

102. *Action of hydrochloric acid upon metals.*—Those metals which have the strongest attraction for oxygen will also generally have the strongest attraction for chlorine, so that in respect to their capability of decomposing hydrochloric acid, they may be ranked in pretty nearly the same order as in their action upon water (p. 19). Since, however, the attraction of chlorine for the metals is generally superior to that of oxygen, the metals are more easily attacked by hydrochloric acid than

* The proportion of acid thus retained by the water varies directly with the atmospheric pressure to which it is exposed during the distillation. A hydrate $HCl.8H_2O$ would contain 20.2 per cent. HCl.

† The realisation of the fact that hydrochloric acid solution behaves similarly to the oxy-acids, led to the abandonment of the view that oxygen is the acid former, and that all acids must contain this element. The facts quoted with regard to the inactivity of anhydrous HCl seem to indicate that oxygen (as water) is, after all, essential to an acid.

by water, the metal taking the place of the hydrogen, and a chloride of the metal being formed.

Even silver, which does not decompose water at any temperature, is dissolved, though very slowly, by boiling concentrated hydrochloric acid, the chloride of silver formed being soluble in the strong acid, though it may be precipitated by adding water.

Gold and platinum, however, are not attacked by hydrochloric acid; but if a little free chlorine be present, it converts them into chlorides.

Iron and zinc decompose the acid very rapidly in the cold, forming ferrous chloride and zinc chloride respectively, and liberating hydrogen; $Fe + 2HCl = FeCl_2 + H_2$.

When potassium or sodium is exposed to hydrochloric acid gas, it immediately becomes coated with a white crust of chloride, which partly protects the metal from the action of the gas; but when these metals are heated to fusion in hydrochloric acid gas, they burn vividly; $Na + HCl = NaCl + H$.

The composition of hydrogen chloride may be exhibited by confining a measured volume of the gas over mercury (see Fig. 106, p. 130), and passing up a freshly cut pellet of sodium. On gently agitating the tube, the gas diminishes in volume, and after a time will have contracted to one-half, and will be found to have all the properties of hydrogen. This result confirms that obtained by synthesis, as described above, that 2 volumes of hydrogen chloride contain 1 volume of hydrogen and 1 volume of chlorine.

The electrolysis of hydrochloric acid, which leads to the same conclusion, has been described at p. 16.

103. *Action of hydrochloric acid upon metallic oxides.*—As a general rule, it may be stated that, when hydrochloric acid acts upon the oxide of a metal, the results are water and a chloride of the metal, in which each atom of oxygen in the oxide has been displaced by 2 atoms of chlorine.

Thus, silver oxide acted on by hydrochloric acid gas gives water and silver chloride; $Ag_2O + 2HCl = H_2O + 2AgCl$.

Suboxide of copper (cuprous oxide) yields water and subchloride of copper (cuprous chloride); $Cu_2O + 2HCl = H_2O + Cu_2Cl_2$.

Ferric oxide gives water and ferric chloride; $Fe_2O_3 + 6HCl = 3H_2O + Fe_2Cl_6$.

With stannic oxide, water and stannic chloride are obtained; $SnO_2 + 4HCl = 3H_2O + SnCl_4$.

Antimonious oxide is converted into water and antimonious chloride; $Sb_2O_3 + 6HCl = 3H_2O + 2SbCl_3$.

104. In cases where the corresponding chloride does not exist, or is not stable under the conditions of the experiment, a chloride is formed containing less chlorine than is equivalent to the oxygen in the oxide, and the balance is evolved in the free state. Thus, when manganese sesquioxide and dioxide are heated with hydrochloric acid—

$$Mn_2O_3 + 6HCl = 3H_2O + 2MnCl_2 + Cl_2;$$
$$MnO_2 + 4HCl = 2H_2O + MnCl_2 + Cl_2.$$

It would seem that Mn_2Cl_6 and $MnCl_4$, corresponding with Mn_2O_3 and MnO_2 respectively, are first formed and that these decompose into the stable chloride, $MnCl_2$, and chlorine.

Chromic anhydride, a chloride corresponding with which is not known

to exist, when heated with hydrochloric acid, yields chromic chloride and chlorine; $2CrO_3 + 12HCl = 6H_2O + Cr_2Cl_6 + Cl_6$.

Most metallic oxides containing 1 atom of oxygen have a corresponding chloride of a stable character, but the higher oxides less frequently form corresponding chlorides endowed with any stability. *Basic oxides* rarely evolve chlorine from hydrochloric acid. When an oxide gives off chlorine on boiling with hydrochloric acid it is probably a *peroxide* or an *acid oxide*, that is, an oxide containing more oxygen than suffices to form a base with the metal. Thus, the basic oxide of manganese is MnO, which dissolves in HCl with evolution of chlorine; but the dioxide MnO_2, or MnO.O, contains an extra atom of oxygen which is able to oxidise HCl; $2HCl + O = H_2O + Cl_2$.

Compounds of Chlorine with Oxygen.

105. It is worthy of notice, that whilst chlorine and hydrogen so readily unite, there is no method by which chlorine can be made to combine in a direct manner with oxygen, the compounds of these elements having been hitherto obtained only by indirect processes. An excellent illustration is thus afforded of the fact, that the more closely substances resemble each other in their chemical relations, the less will be their tendency to combine; for chlorine and oxygen are both highly electro-negative bodies, and therefore, having both a powerful attraction for the electro-positive hydrogen, their attraction for each other is of a very low order.

Three oxides of chlorine, Cl_2O, ClO_2 and Cl_2O_7, and four oxyacids of chlorine, HClO, $HClO_2$, $HClO_3$, and $HClO_4$, are known.

106. **Hypochlorous anhydride** or **chlorine monoxide** (Cl_2O), is of some practical interest in connection with *chloride of lime*, *chloride of soda*, and other bleaching compounds. It is prepared by passing dry chlorine gas over dry precipitated mercuric oxide, and condensing the product in a tube surrounded with a mixture of ice and salt; $HgO + Cl_4 = HgCl_2 + Cl_2O$.

The hypochlorous anhydride is thus obtained as a dark brown liquid, which boils at 6° C., evolving a yellow gas thrice as heavy as air, and having a very powerful and peculiar odour. This gas is remarkably explosive, the heat of the hand having been known to cause its separation into its constituents, when 2 volumes of the vapour yield 2 volumes of chlorine and 1 volume of oxygen. As might be expected, most substances which have any attraction for oxygen or chlorine, and therefore raise the temperature of the gas by combining with a portion of its oxygen or chlorine, will decompose the gas, sometimes with explosive violence. This instability of chlorine monoxide is only to be expected from the fact that it *evolves* heat (17,800 gram units for 87 grams) in its decomposition, and is therefore an endothermic compound, *i.e.*, one which could only be formed from its elements by the absorption of heat. It is generally true that *endothermic compounds can be exploded by a shock*, such as that caused by a sudden rise of temperature. Even hydrochloric acid decomposes Cl_2O: 1 volume of chlorine monoxide is entirely decomposed by 2 volumes of hydrochloric acid, yielding water and chlorine; $Cl_2O + 2HCl = H_2O + Cl_4$. Chlorine monoxide is a powerful bleaching agent, both its chlorine and oxygen acting upon the colouring matter in the manner explained at page 175.

Hypochlorous anhydride is absorbed in large quantity by water (200 vols. in 1 vol.); the solution is supposed to contain *hypochlorous acid*, HClO or Cl.OH, for $H_2O + Cl_2O = 2HClO$; but HClO has not been obtained in the separate state. The solution may be very readily prepared by shaking mercuric oxide with water in a bottle of chlorine as long as the gas is absorbed. The greater part of the mercuric chloride which is produced combines with the excess of oxide to form a brown insoluble oxychloride, $HgO.HgCl_2$, whilst the hypochlorous acid and a little mercuric chloride remain in solution. A solution of the acid, containing calcium chloride, may also be obtained by passing Cl into $CaCO_3$ suspended in water; $CaCO_3 + H_2O + Cl_4 = CaCl_2 + 2HClO + CO_2$. This solution is a most powerful oxidising and bleaching agent, since it readily decomposes into HCl and O; it erases writing ink immediately, and does not corrode the paper if it be carefully washed. Printing ink, which contains lamp black and grease, is not bleached by hypochlorous acid, so that this solution is very useful for removing ink stains from books, engravings, &c. For the same weight of Cl it is twice as effective as chlorine water; $2HClO = HCl + O_2$; $H_2O + Cl_2 = 2HCl + O$.

The action of some metals and their oxides upon solution of hypochlorous acid is instructive. Iron seizes upon the oxygen, whilst the chlorine is liberated; copper takes both the oxygen and chlorine; whilst silver combines with the chlorine, and liberates oxygen. Mercury yields, on shaking, the brown mercuric oxychloride. This distinguishes solution of HClO from chlorine water. Oxide of lead (PbO) removes the oxygen, becoming peroxide of lead (PbO_2), and liberating chlorine, but oxide of silver converts the chlorine into chloride of silver, and liberates the oxygen; $Ag_2O + Cl_2O = 2AgCl + O_2$.

Hypochlorous acid is formed when a weak solution of hydrogen peroxide is added to a large excess of chlorine water; $Cl_2 + H_2O_2 = 2HClO$. With an excess of the peroxide, $HClO + H_2O_2 = HCl + H_2O + O_2$.

The salts of hypochlorous acid, or *hypochlorites*, are obtained in solution by neutralising hypochlorous acid with bases, only a few of them are known in a pure state. They are decomposed even by carbonic acid, with liberation of hypochlorous acid.

When chlorine is passed into a solution of a metallic hydroxide the hypochlorite and chloride of the metal are obtained, $2NaOH + Cl_2 = NaOCl + NaCl + HOH$; the hypochlorite may be supposed to be formed by metalepsis (p. 174) with the hydroxide $NaOH + Cl_2 = NaOCl + HCl$, the hydrochloric acid thus formed being neutralised by another portion of NaOH.

By the addition of any acid which can liberate hydrochloric acid, and therefore also the much feebler hypochlorous acid, to the solution containing the chloride and hypochlorite, chlorine will be evolved since hydrochloric and hypochlorous acids react, the hydrogen being oxidised and the chlorine set free, $HCl + HClO = H_2O + Cl_2$. If only a small proportion of acid is added to the solution of hypochlorite and chloride, the hypochlorous acid will alone be liberated, and may be distilled together with the water.

When the solution of a hypochlorite is boiled, it undergoes self-oxidation, that is, one part of the hypochlorite loses oxygen, becoming chloride, whilst the remainder is oxidised by this oxygen to chlorate; $3KClO = KClO_3 + 2KCl$. This change is turned to practical account in the manufacture of potassium chlorate. It is much hindered by the presence of an excess of alkali. The solution of hypochlorous acid itself,

when exposed to light, is decomposed into chloric acid and free chlorine; $5HClO = HClO_3 + 2H_2O + Cl_4$.

A solution of hypochlorous acid may be obtained by adding boric acid in excess to a solution of chloride of lime.

107. *Chloride of lime* or *bleaching powder*, or *calx chlorata*, is prepared by passing chlorine gas into boxes of lead or stone in which a quantity of moist slaked lime is spread out. The temperature is not allowed to rise above 25° C. (77° F.), which is ensured by acting upon the fresh lime with chlorine diluted by air. The lime absorbs nearly half its weight of chlorine, and forms a white powder, which has a very peculiar smell, somewhat different from that of chlorine.

The formula of chloride of lime is generally written CaCl.OCl.

The constitution of chloride of lime is not known with certainty. When the calcium hydroxide, $Ca(OH)_2$, is acted on by chlorine, the simplest reaction would be $Ca(OH)_2 + Cl_2 = CaCl(OCl) + H_2O$, according to which the chloride of lime would result from the substitution of Cl for one of the OH groups, and the removal of the H of the other as H_2O, this atom of H being then exchanged for Cl; but this would require the calcium hydroxide to absorb nearly an equal weight of chlorine, whereas the amount is not much more than half this quantity. This deficiency is partly explained by the fact that a small portion of the lime is not attacked by the chlorine.

Practically, the constitution of chloride of lime itself is of less importance than that of the solution obtained by treating it with water, which is generally admitted to contain calcium hypochlorite, $Ca(OCl)_2$, and calcium chloride, $CaCl_2$, with some calcium hydroxide, $Ca(OH)_2$, of which a quantity is left in the undissolved residue. The decomposition of chloride of lime by water should be represented by the following equation: $2CaCl(OCl) = CaCl_2 + Ca(OCl)_2$.

If the solution of chloride of lime is added to blue litmus, it exerts little bleaching action; but on adding a little acid (sulphuric, for example), the blue colour is discharged, the acid setting free the chlorine, which acts upon the colouring matter—

$$Ca(OCl)_2 + CaCl_2 + 2H_2SO_4 = 2CaSO_4 + 2H_2O + Cl_4.$$

Solution of *chloride of lime.*

Even carbonic acid will develop the bleaching property of chloride of lime (by liberating hypochlorous acid), so that the above mixture may be decolorised by breathing into it through a glass tube.

When chloride of lime is used for bleaching on the large scale, the stuff to be bleached is first thoroughly cleansed from any grease or *weaver's dressing*, by boiling it in lime-water and in a weak solution of soda, and is then immersed in a weak solution of the chloride of lime. This, by itself, however, exerts very little action upon the natural colouring matter of the fibre, and the stuff is therefore next immersed in very dilute sulphuric acid, when the colouring matter is so far altered as to become soluble in the alkaline solution in which the fabric is next immersed, and a repetition of these processes, followed by a thorough rinsing, generally perfects the bleaching.

The property possessed by acids of liberating chlorine from the chloride of lime is applied, in calico-printing, to the production of white patterns upon a red ground. The stuff having been dyed with Turkey-red, the pattern is imprinted upon it with a *discharge* consisting of an acid (tartaric, phosphoric, or arsenic) thickened with gum. On passing the fabric through a bath of weak chloride of lime, the colour is discharged only at those parts to which the acid has been applied, and where, consequently, chlorine is liberated.

Chloride of lime is one of the most convenient forms in which to apply chlorine for the purposes of fumigating and disinfecting. If a cloth saturated with the solution be suspended in the air, the carbonic acid gas in the latter causes a slow evolution of hypochlorous acid, which is even a more powerful disinfectant than chlorine itself. In extreme cases, where a rapid evolution of chlorine is required, the bleaching powder is placed in a plate, and diluted sulphuric acid is poured over it, or the powder may be mixed with half its weight of powdered alum in a plate, when a pretty rapid and regular escape of chlorine will ensue.

The best bleaching powder contains about 37 per cent. of chlorine which can be liberated ("available chlorine") in the above processes. It is liable to decomposition when kept, evolving oxygen, and becoming converted into calcium chloride, which attracts moisture greedily, and renders the bleaching powder deliquescent. It has been known to shatter the glass bottle in which it was preserved, in consequence of the accumulation of oxygen; * $CaOCl_2 = CaCl_2 + O$.

When a solution of a salt of manganese or cobalt is added to solution of chloride of lime, a black precipitate of MnO_2 or Co_2O_3 is obtained. If this precipitate be boiled with an excess of solution of chloride of lime, it causes a rapid disengagement of oxygen, in some manner that has not yet been clearly explained. Large quantities of oxygen are easily obtained by adding a few drops of solution of cobalt nitrate to solution of chloride of lime, and applying a gentle heat.

Old chloride of lime always contains calcium chlorate; $6CaOCl_2 = 5CaCl_2 + Ca(ClO_3)_2$.

Sodium hypochlorite, which is very useful for removing ink, is prepared in solution by decomposing solution of chloride of lime with solution of sodium carbonate, and separating the calcium carbonate by filtration. The solution is generally called "chloride of soda" (*liquor sodæ chloratæ. Eau de Javelle*).

108. **Chloric acid** ($HClO_3$ or $ClO_2(OH)$).—This acid is appropriately studied here, since its salts are usually obtained by the decomposition of the hypochlorites. The only chlorate which possesses any great practical importance is potassium chlorate ($KClO_3$), which is largely employed as a source of oxygen, as an ingredient of several explosive compositions, and in the manufacture of lucifer matches.

Potassium chlorate, or *chlorate of potash*.—The simplest method of obtaining this salt consists in passing an excess of chlorine rapidly into a strong solution of potash when the liquid becomes hot enough to decompose the hypochlorite first formed into potassium chloride, which remains in solution, and potassium chlorate, which is deposited in tabular crystals, the ultimate result being expressed by the equation—

$$6KOH + Cl_6 = KClO_3 + 5KCl + 3H_2O.$$

If potassium carbonate or a weak solution of potash be employed, the liquid will require boiling after saturation with chlorine, in order to convert the hypochlorite into chlorate.

The following proportions will be found convenient for the preparation of potassium chlorate on the small scale as a laboratory experiment. 20 grms. of potassium

* When rapidly made and hastily packed, it has been known to become so hot as to set fire to the casks.

carbonate are dissolved, in a beaker, with 60 c.c. of water. 40 grms. of NaCl are mixed with 30 grms. of MnO_2, and very gently heated in a flask with a mixture of 40 c.c. of strong H_2SO_4 and 110 c.c. of water, the evolved chlorine being passed through a rather wide bent tube into the solution of potassium carbonate.

At first no action appears to occur, although the solution absorbs the chlorine; because the first portion of that gas converts the potassium carbonate into a mixture of potassium hypochlorite, potassium chloride, and hydropotassium carbonate, some crystals of which will probably be deposited; $2K_2CO_3 + Cl_2 + H_2O = KCl + KOCl + 2KHCO_3$. On continuing to pass chlorine, these crystals will redissolve, and brisk effervescence will be caused by the expulsion of the carbonic acid gas; $2KHCO_3 + Cl_2 = KCl + KOCl + H_2O + 2CO_2$. When this effervescence has ceased, and the chlorine is no longer absorbed by the liquid, the change is complete, the ultimate result being represented by the equation $K_2CO_3 + Cl_2 = KCl + KOCl + CO_2$. The solution (which often has a pink colour, due to a little potassium ferrate) is now poured into a dish, boiled for two or three minutes, filtered, if necessary, from any impurities (silica, &c.) derived from the potassium carbonate, and set aside to crystallise. The ebullition has converted the potassium hypochlorite into chlorate and chloride of potassium; $3KOCl = KClO_3 + 2KCl$. The latter, being soluble in about three times its weight of cold water, is retained in the solution, whilst the chlorate, which would require about sixteen times its weight of cold water to hold it dissolved, is deposited in brilliant rhomboidal tables. These crystals may be collected on a filter, and purified from the adhering solution of potassium chloride by pressure between successive portions of filter-paper. If they be free from chloride, their solution in water will not be changed by silver nitrate, which would yield a milky precipitate of silver chloride if potassium chloride were present. Should this be the case, the crystals must be redissolved in a small quantity of boiling water, and recrystallised.

The above processes for preparing potassium chlorate are far from economical, since five-sixths of the potash are converted into chloride, being employed merely to furnish oxygen to convert the chlorine into chloric acid. In manufacturing the chlorate upon the large scale, a much cheaper material, lime, is used to furnish the oxygen. The lime is mixed with water, and saturated with chlorine gas in closed leaden tanks; $2Ca(OH)_2 + Cl_4 = Ca(OCl)_2 + CaCl_2 + 2H_2O$. The liquid is boiled down, when the calcium hypochlorite is decomposed into calcium chlorate and chloride; $3Ca(OCl)_2 = Ca(ClO_3)_2 + 2CaCl_2$. The calcium chlorate is now decomposed by boiling with potassium chloride, when it yields calcium chloride which remains in solution, and potassium chlorate which crystallises as the solution cools—

$$Ca(ClO_3)_2 + 2KCl = CaCl_2 + 2KClO_3.$$

Chlorate of potash is also made electrolytically as mentioned in the section on potassium.

Chloric acid ($HClO_3$) may be procured by decomposing a solution of potassium chlorate with hydrofluosilicic acid, when the potassium is deposited as an insoluble silico-fluoride, and chloric acid is found in the solution; $2KClO_3 + H_2SiF_6 = 2HClO_3 + K_2SiF_6$.

On evaporating the solution below 38° C., the chloric acid is obtained as a yellow liquid, $HClO_3.7Aq$, with a peculiar pungent smell.

In its chemical characters, chloric acid bears a very strong resemblance to nitric acid, but is far more easily decomposed. It cannot even be kept unchanged for any length of time, and at temperatures above 40° C. it is decomposed into perchloric acid, chlorine, and oxygen; $4HClO_3 = 2HClO_4 + H_2O + Cl_2 + O_3$.

Chloric acid is one of the most powerful oxidising agents: a drop of it will set fire to paper, and it oxidises phosphorus (even the amorphous variety) with explosive violence. Like hypochlorous acid it will oxidise

hydrochloric acid; $HClO_3 + 5HCl = 3H_2O + Cl_6$.* Yet it dissolves Zn with evolution of H.

109. *Chlorates.*—Chloric acid, like nitric, is monobasic, containing only one atom of hydrogen which can be exchanged for a metal. The chlorates resemble the nitrates in their oxidising powder, but generally act at lower temperatures, in consequence of the greater facility with which the chlorates part with their oxygen.

A grain or two of potassium chlorate, rubbed in a mortar with a little sulphur, for example, detonates violently, evolving a powerful odour of chloride of sulphur. Potassium chlorate and sulphur were used in some of the first percussion caps, but being found to corrode the nipple of the gun, they gave place to the *anti-corrosive caps* containing mercuric fulminate.

If a little powdered chlorate be mixed on a card with some black antimony sulphide, and wrapped up in paper, the mixture will detonate when struck with a hammer. The earliest lucifer matches were tipped with a mixture of potassium chlorate, antimony sulphide, and starch, and were kindled by drawing them briskly through a doubled piece of sand-paper.

A mixture of potassium chlorate and lead ferrocyanide is used in toy detonating crackers.

At high temperatures the chlorates act violently upon combustible bodies. A little potassium chlorate sprinkled upon red-hot coal causes a very violent deflagration. If a little of the chlorate be melted in a deflagrating spoon, and plunged into a bottle or flask containing coal gas, the salt burns with great brilliancy, its oxygen combining with the carbon and hydrogen in the gas, which becomes in this case the *supporter of combustion.*

Potassium chlorate is much used in the manufacture of fireworks, especially as an ingredient of coloured fire compositions, which generally consist of potassium chlorate mixed with sulphur, and with some metallic compound, to produce the desired colour in the flame.

They are not generally made of the best quality on the small scale, from want of attention to the very finely powdered state of the ingredients, the absence of all moisture, and the most intimate mixture, but if these precautions are attended to, the following prescriptions will give very good coloured fires:

Red fire.—40 grains of strontium nitrate, thoroughly dried over a lamp, are mixed with 10 grains of potassium chlorate, and reduced to the finest possible powder. *In another mortar* 13 grains of sulphur are mixed with 4 grains of black sulphide of antimony (crude antimony). The two powders are then placed upon a sheet of paper, and very intimately mixed with a bone knife, avoiding any great pressure. A little heap of the mixture touched with a red-hot iron ought to burn with a uniform red flame, the colour being due to the strontium.†

Blue fire.—15 grains of potassium chlorate are mixed with 10 grains of potassium nitrate and 30 grains of oxide of copper, in a mortar. The finely powdered mixture is transferred to a sheet of paper, and mixed, by a bone knife, with 15 grains of sulphur. The colour of the fire is given chiefly by the copper.

Green fire.—10 grains of barium chlorate are mixed with 10 grains of barium nitrate in a mortar, and afterwards on paper with 12 grains of sulphur. The barium is the cause of the bright green colour of the flame.

These compositions are rather dangerous to keep, since they are liable to spontaneous combustion.

White gunpowder is a mixture of two parts of potassium chlorate with one part of dried yellow prussiate of potash, and one part of sugar, which explodes very easily under friction or percussion.

The decomposition $KClO_3 = KCl + O_3$ is exothermic, 9700 calories being evolved per gram molecule of potassium chlorate. If the chlorate be

* Perchloric acid and chlorine peroxide are also produced.

† The red fire made by pyrotechnists commonly contains charcoal 1 part, shellac 4 parts, sulphur 8 parts, potassium chlorate 12 parts, strontium nitrate 40 parts.

heated to the point at which it begins to decompose, and a little ferric oxide be thrown into it, enough heat will be evolved to bring the mass to a red heat, although the ferric oxide is not oxidised. This evolution of heat must of course contribute to increase the energy of explosive mixtures containing the chlorate, and may be accounted for on the supposition that the heat evolved by the combination of the K with the Cl to form KCl exceeds that which is absorbed in effecting the chemical decomposition of the chlorate.

110. **Perchloric acid** ($HClO_4$ or $ClO_3(OH)$), is obtained by evaporating, at a boiling heat, the solution of chloric acid obtained by decomposing potassium chlorate with hydrofluosilicic acid (see page 185), when the chloric acid is decomposed into perchloric acid, chlorine, and oxygen; $4HClO_3 = 2HClO_4 + H_2O + Cl_2 + O_3$. The pure acid is best obtained by distilling potassium perchlorate (see below) with four times its weight of strong H_2SO_4 in a vacuum. At 56 mm. pressure it boils at 39° C.

The pure perchloric acid is a colourless, very heavy liquid (sp. gr. 1.764 at 22° C.), which soon becomes yellow from decomposition. It cannot be kept for any length of time, but it is more stable than any of the other oxyacids of chlorine. When heated, it decomposes, often with explosion. In its oxidising properties it is more powerful than chloric acid. It burns the skin in a very serious manner, and sets fire to paper, charcoal, &c., with explosive violence. This want of stability, however, belongs only to the pure acid. If water be added to it, heat is evolved, and a crystalline acid, $HClO_4.H_2O$, melting at 50° C., may be obtained. Diluted perchloric acid is much more stable than the pure acid; it does not even bleach, but reddens litmus in the ordinary way. It dissolves Zn with evolution of H.

Perchloric acid is monobasic. The *perchlorates* are decomposed by heat, evolving oxygen, and leaving chlorides; thus—$KClO_4 = KCl + O_4$.

The potassium perchlorate is one of the least soluble of the potassium salts, requiring 150 times its weight of cold water to dissolve it. It is always formed in the first stage of the decomposition of potassium chlorate by heat; $2KClO_3 = KClO_4 + KCl + O_2$.

If a few crystals of potassium chlorate be heated in a test-tube, they first melt to a perfectly clear liquid, which soon evolves bubbles of oxygen. After a time the liquid becomes pasty, and if the contents of the tube, after cooling, be dissolved by boiling with water, the latter will deposit, as it cools, crystals of potassium perchlorate. These are readily distinguished from the chlorate by their not yielding a yellow gas (ClO_2) when treated with strong sulphuric acid. Neither perchloric acid nor any of its salts is applied to any useful purpose.

111. **Chlorine dioxide** or **chlorine peroxide** (ClO_2) is dangerous to prepare and examine on account of its great instability and violently explosive character. It is obtained by the action of strong sulphuric acid upon potassium chlorate—

$$3KClO_3 + 2H_2SO_4 = KClO_4 + 2KHSO_4 + 2ClO_2 + H_2O.$$

It is a bright yellow gas, with a chlorous and somewhat aromatic smell, and sp. gr. 2.32; condensable to a red, very explosive liquid (b.p. 9° C.). The gas is gradually decomposed into its elements by exposure to light, and a temperature of 60° C. causes it to decompose with violent explosion into a mixture of chlorine and oxygen, the volume of which is one and a half times that of the compound.

On a small scale, chlorine peroxide may be prepared with safety by pouring a little strong sulphuric acid upon one or two crystals of potassium chlorate, in a test-tube supported in a holder. The crystals at once acquire a red colour, which gradually diffuses itself through the liquid, and the bright yellow gas collects in the tube. If heat be applied, the gas will explode, and the colour and odour of chlorine peroxide will be exchanged for those of chlorine. If the chlorate employed in this experiment contains potassium chloride, explosion often happens in the cold, since the hydrochloric acid evolved by the action of the acid upon that salt decomposes a part of the chlorine peroxide, and thus provokes the decomposition, of the remainder.

ClO_2 is easily absorbed by water, forming chlorous and chloric acids; the solution has powerful bleaching properties. Combustible bodies, such as sulphur and phosphorus, decompose the gas, as might be expected, with great violence. This powerful oxidising action of chlorine peroxide upon combustible substances appears to be the cause of the property possessed by mixtures of such substances with potassium chlorate, to inflame when touched with strong sulphuric acid.

If a few crystals of potassium chlorate be thrown into a glass of water (Fig. 153), one or two small fragments of phosphorus dropped upon them, and some strong sulphuric acid poured down a funnel tube to the bottom of the glass, the chlorine peroxide will inflame the phosphorus with bright flashes of light and slight detonations.

Fig. 153.

Powdered sugar mixed with potassium chlorate on paper, will burn brilliantly when touched with a glass rod dipped in strong sulphuric acid. Matches may be prepared, which inflame when moistened with sulphuric acid, by dipping the end of splinters of wood in melted sulphur, and, when cool, tipping them with a mixture of 5 grains of sugar and 15 grains of potassium chlorate made into a paste with 4 drops of water. When dry, they may be fired by dipping them into a bottle containing asbestos moistened with strong sulphuric acid. These matches, under the names of Eupyrion and Vesta matches, were used before the introduction of phosphorus into general use. The Promethean light was an ornamental scented paper spill, one end of which contained a small glass bulb of sulphuric acid surrounded with a mixture of chlorate and sugar, which inflamed when the end of the spill was struck or squeezed, so as to break the bulb containing the sulphuric acid. The paper was waxed in order to make it inflame more easily. Percussion fuses, &c., have been often constructed upon a similar principle.

Chlorous acid, $HClO_2$, or $ClO(OH)$, is contained, together with chloric acid, in the aqueous solution of chlorine peroxide ($2ClO_2 + H_2O = HClO_2 + HClO_3$) which thus resembles nitric peroxide in not being a separate anhydride.

The chlorous acid may be separated by neutralising the solution with potash and evaporating until the potassium chlorate crystallises, leaving the chlorite ($KClO_2$) in solution. Little is known about the acid or its salts; they readily undergo self-oxidation, like hypochlorous acid and its salts, yielding chloric acid and chlorates.

112. *Euchlorine*, the deep yellow, dangerously explosive gas evolved by the action of strong HCl upon $KClO_3$, appears to be a mixture of chlorine peroxide with chlorine. It is resolved by explosion into 2 vols. Cl and 1 vol. O. Mercurous chloride absorbs Cl from it, leaving ClO_2. Hence its production may be explained by the equation, $4KClO_3 + 12HCl = 4KCl + 6H_2O + 3ClO_2 + Cl_2$.

Chlorine heptoxide, presumably Cl_2O_7, is obtained by dropping perchloric acid on to phosphoric anhydride cooled below $-10°$ C. and after a day or two warming the retort until the heptoxide distils. It is a colourless volatile oil, boiling at 82° C., and easily exploded. It is probably ***perchloric anhydride.***

Chlorides of Carbon.

113. It has already been seen that chlorine has no direct attraction for carbon, the two elements not being known to enter into direct combination; but several chlorides of carbon may be obtained by the action of chlorine upon other compounds of carbon, particularly by metalepsis with hydrocarbons.

Carbon tetrachloride, CCl_4, has been mentioned (p. 174) as the final result of the action of chlorine upon marsh gas (CH_4) and upon chloroform ($CHCl_3$). It is easily obtained in large quantity, by passing chlorine (dried by passage through a tube containing pumice wetted with strong H_2SO_4) (Fig. 154), through a bottle containing carbon bisulphide, and afterwards through a porcelain tube, filled with fragments of broken porcelain and maintained at a red heat by a gas furnace; the products are condensed in a bottle surrounded by ice. A mixture

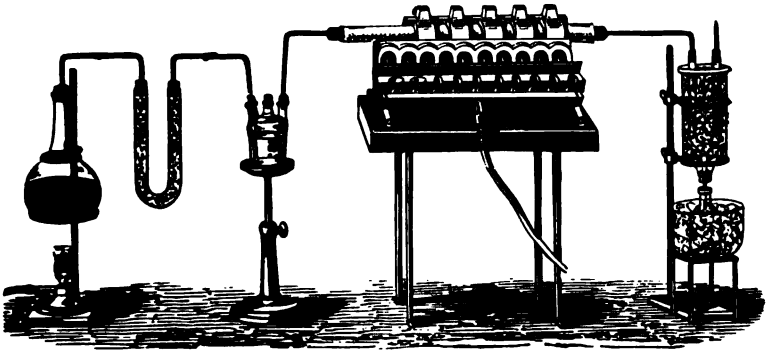


Fig. 154.—Preparation of carbon tetrachloride.

of carbon tetrachloride and sulphur dichloride is thus obtained; $CS_2 + Cl_6 = CCl_4 + S_2Cl_2$. This is shaken with potash, whereupon the sulphur dichloride is decomposed and dissolved, whilst the carbon tetrachloride separates and falls to the bottom. The two layers having been separated by a separating funnel (p. 139), the tetrachloride may be purified by distillation.

Another method of preparing CCl_4 consists in distilling carbon bisulphide with antimonic chloride in a stream of chlorine.

Carbon tetrachloride is a colourless liquid, much heavier than water (sp. gr. 1.6), having a peculiar odour, and boiling at 77° C. It may be solidified at −23° C. The tetrachloride is insoluble in water, but dissolves in alcohol and in ether. It is a very useful solvent for fats, and also finds application in making dyestuffs.

It will be obvious that since the number of hydrocarbons is very large there must be a considerable number of chlorides of carbon obtained by the complete substitution of chlorine for hydrogen, generally by metalepsis. Some of these are of very high molecular weight, such as octachloronaphthalene $C_{10}Cl_8$, obtained from naphthalene $C_{10}H_8$.

Carbon trichloride, *perchlorethane* or *hexachlorethane*, C_2Cl_6, is produced by treating Dutch liquid (p. 143) with excess of chlorine in sunlight.

It is a white crystalline solid, melting at 187° C. By treatment with nascent hydrogen (zinc and sulphuric acid) it yields *carbon dichloride*, or *tetrachlorethylene*, C_2Cl_4, a colourless liquid which boils at 121° C.

114. **Carbonyl chloride**, *carbon oxychloride*, or *phosgene gas*, $COCl_2$, is produced by the direct combination of equal volumes of carbonic oxide and chlorine gases under the influence of sunlight (whence its last name), when the mixture condenses to half its volume of a colourless gas, condensable by cold (b.p. 8.4° C.), having a very peculiar pungent smell, and fuming strongly when exposed to moist air by decomposing the moisture and producing hydrochloric acid; $COCl_2 + H_2O = CO_2 + 2HCl$. It is decomposed by alkalies, producing chlorides and carbonates. It is used in the manufacture of some artificial dyestuffs.

$COCl_2$ may also be prepared by passing a mixture of equal volumes of CO and Cl through a long tube filled with granulated animal charcoal, which favours the combination of the gases; or by passing dried carbonic oxide through antimony pentachloride; $SbCl_5 + CO = COCl_2 + SbCl_3$.

Phosgene gas has also been obtained by heating carbon tetrachloride with phosphoric anhydride, in a sealed tube; $3CCl_4 + P_2O_5 = 2POCl_3 + 3COCl_2$; and by heating chloroform with sulphuric acid and potassium dichromate.

A convenient method for preparing phosgene gas consists in dropping fuming sulphuric acid (containing 80 per cent. SO_3) down an inverted condenser into a flask in which carbon tetrachloride is boiling. The gas escapes through a side tube at the top of the condenser and is washed by passage through strong H_2SO_4; $CCl_4 + 2SO_3 = COCl_2 + S_2O_5Cl_2$ (*pyrosulphuryl chloride*).

115. **Nitrogen chloride** is the name usually given to the very explosive compound before referred to as being produced by the action of chlorine on ammonium chloride. The oily liquid thus produced is a mixture of several compounds which have been formed from the NH_4Cl by the substitution of chlorine for hydrogen. Nitrogen chloride, NCl_3, is the most explosive constituent of the mixture, and can be isolated by a process attended with considerable danger.

It is a yellow, heavy, oily liquid (sp. gr. 1.7), which volatilises easily, yielding a vapour of very characteristic odour, which affects the eyes. When heated to about 93° C. it explodes with great violence, emitting a loud report and a flash of light.* Its instability is, of course, attributable to the feeble attraction which holds its elements together; and the violence of the explosion, to the sudden expansion of a small volume of the liquid into a large volume of nitrogen and chlorine.

As might be expected, its explosion is at once brought about by contact with substances which have an attraction for chlorine, such as phosphorus and arsenic; the oils and fats cause its explosion, probably by virtue of their hydrogen; oil of turpentine explodes it with greater certainty than the fixed oils. Alkalies also decompose it violently; whilst acids, having no action upon the chlorine, are not so liable to explode it. At 71° C. this substance has actually been distilled without explosion.

Although practically unimportant, the violently explosive properties of this substance render it so interesting that it may be well to give some directions for its safe preparation, which may be effected by the action of solution of hypochlorous acid upon ammonium chloride.

Fifty grains of red oxide of mercury are very finely powdered and thrown into a pint bottle of chlorine together with ½ oz. of water. The stopper is replaced, and the bottle well shaken, loosening the stopper occasionally, as long as the chlorine is absorbed. The solution of hypochlorous acid thus produced is filtered from the residual mercuric oxychloride, and poured into a clean *thumb-glass*

* It is said to absorb 38,478 gram units of heat per equivalent, in the process of formation, and would therefore disengage that amount of heat in the act of decomposition.

(Fig. 155). A lump of ammonium chloride weighing 20 grains is then dropped into the solution, and the glass is placed under a stout wooden box. After the lapse of twenty minutes, the chloride of nitrogen may be exploded by inserting, through a hole in the box, a stick dipped in turpentine, fixed at right angles to a longer stick. The glass will be shattered into very small fragments.

Fig. 155.

116. **Aqua regia.**—This name has been bestowed upon the mixture of 1 measure of nitric, and 3 measures of hydrochloric acid (*nitromuriatic acid*), which is employed for dissolving gold, platinum, and other metals which are not soluble in the separate acids. A little gold leaf placed in hydrochloric and nitric acids contained in separate glasses remains unaffected even on warming the acids; but if the contents of the glasses be mixed, the gold will be immediately dissolved by the chlorine, which is liberated in the action of the acids upon each other; $HNO_3 + 3HCl = 2H_2O + NOCl + Cl_2$.

The **nitrosyl chloride** (NOCl) is a red gas, condensable in a freezing mixture to a dark red liquid, which boils at −8° C. and dissociates above 700° C. It has a very peculiar odour, and is decomposed by contact with water, nitrous acid and hydrochloric acid being produced. Nitrosyl chloride is also produced by mixing 2 volumes of nitric oxide with 1 volume of chlorine; it condenses to a red liquid when cooled. When nitrosyl chloride is passed into oil of vitriol cooled to 0° C., crystals of the acid *nitrosyl sulphate* ($NO{\cdot}HSO_4$) are deposited; $NO{\cdot}Cl + SO_2(OH)(OH) = HCl + SO_2(OH)(ONO)$*.

Nitrosyl sulphate is also obtained by passing SO_2 into nitric acid, or N_2O_3 into sulphuric acid, or by burning a mixture of 1 part of sulphur and 3 parts of nitre in moist air.

Nitrosyl chloride is best prepared by heating nitrosyl sulphate with sodium chloride; $NO{\cdot}HSO_4 + NaCl = NO{\cdot}Cl + NaHSO_4$. It is a useful reagent in organic chemistry.

It has been proposed to manufacture chlorine by oxidising hydrochloric acid with nitric acid as shown by the above equation for the decomposition of *aqua regia*. The mixture of NOCl and Cl_2 is passed through strong sulphuric acid whereby the NOCl is absorbed and HCl evolved in its stead; this is removed from the Cl by passage through water. By diluting the sulphuric acid containing the nitrosyl sulphate and passing air through the liquid, NO_2 is evolved, which may be passed (together with air) into water to form HNO_3. In this way the nitric acid would serve as a carrier of oxygen from the air to the hydrogen of the hydrochloric acid.

Nitrosyl chloride, $NO{\cdot}Cl$, is an example of a large class of compounds known as *acid chlorides* or *chloranhydrides*. An acid chloride is formed by the substitution of Cl for OH in an acid; thus nitrosyl chloride is formed from nitrous acid, $NO{\cdot}OH$. The reaction which most generally produces an acid chloride is that between an oxy-acid and phosphoric chloride, PCl_5 (see *Phosphorus*); if R represent the group of atoms combined with OH in an acid, this reaction may be expressed by the equation, $R{\cdot}OH + PCl_5 = R{\cdot}Cl + POCl_3 + HCl$, or, since the acid residue may be combined with several OH groups, $R(OH)_n + nPCl_5 = RCl_n + nPOCl_3 + nHCl$. It is from this fact, namely, that for every atom of chlorine introduced into an acid by the action of phosphoric chloride, one atom of oxygen and one atom of hydrogen are removed (as $POCl_3$ and HCl respectively), that the inference is drawn that *the hydrogen in an oxyacid exists in the form of hydroxyl groups*. For it

* In this formula for nitrosyl sulphate the nitrosyl group is exchanged for hydrogen in one of the hydroxyl groups of sulphuric acid. Some chemists regard the compound as *nitrosulphuric* or *nitrosulphonic* acid, that is, sulphuric acid in which NO_2 has been substituted for H :—$SO_2(OH)(NO_2)$.

is obvious that a monovalent atom like Cl can only be substituted for another monovalent atom or a monovalent radicle, so that if O and H are together exchanged for Cl they must be present as –OH; were they present independently of each other they would represent three atom-fixing powers (–O– and H–), and could not be exchanged for the monovalent atom Cl. It will be found, particularly in organic chemistry, that acids frequently contain O and H, for which Cl cannot be substituted, and therefore exist in some other relationship to the molecule than that represented by –OH.

The characteristic behaviour of acid chlorides is, that when brought into contact with water they exchange their chlorine for hydroxyl, and are converted into the acids from which they were derived; $RCl_n + nHOH = R(OH)_n + nHCl$. It is because these chlorides form acids, in this way, when brought in contact with water, that they are also termed chloranhydrides.

It is noteworthy that whilst the acid chlorides yield acid hydroxides and hydrochloric acid by treatment with water, the basic hydroxides, such as NaOH, $Ca(OH)_2$, yield basic chlorides and water by treatment with hydrochloric acid; thus it is instructive to compare the reactions:

$$NO{\cdot}Cl + HOH = NO{\cdot}OH + HCl,$$
and $$NaOH + HCl = NaCl + HOH.$$

Nitroxyl chloride or *nitryl chloride*, NO_2Cl, is the acid chloride from nitric acid, $NO_2.OH$. It is produced by heating NO_2 with Cl, $NO_2 + Cl = NO_2Cl$, and is a yellowish red liquid boiling at 5° C.

Carbonyl chloride, $COCl_2$, is the acid chloride of carbonic acid, $CO(OH)_2$.

BROMINE.

Br = 79.5 parts by weight.

117. It generally happens that elements between which any strong family likeness exists are found associated in nature. This remark particularly applies to the three elements—chlorine, bromine, and iodine—all of which are found in sea water, though the first predominates to such an extent that the others for a long time escaped notice. Bromine was brought to light in the year 1826 by Balard in the examination of *bittern*, which is the liquid remaining after the sodium chloride and some other salts have been made to crystallise by evaporating sea water, which contains bromine in the forms of bromide of magnesium and bromide of sodium.* It has also been extracted from the waters of certain mineral springs, as those of Kreuznach and Kissingen, which contain much larger quantities of bromine, combined with potassium, sodium, or magnesium. Now, almost the sole sources of bromine are the mother-liquors of the salt-works at Stassfurt, and from certain saline springs in the United States.

In extracting the bromine from these waters, advantage is taken of the circumstance that chlorine displaces bromine from its combinations with the metals. After most of the other salts, such as sodium chloride, sodium sulphate, and magnesium sulphate, which are less soluble than the bromides, have been separated from the water by evaporation and

* 4.9 grams of magnesium bromide per gallon have been found in the water of the Irish Sea.

crystallisation, the remaining liquid, containing about 0.3 per cent. of bromine, is run down a tower packed with earthenware balls, where it meets a current of steam conveying chlorine which has been passed into it from a chlorine still. The bromine is liberated from the bromides, the chief of which is magnesium bromide ($MgBr_2 + Cl_2 = MgCl_2 + Br_2$), and passes as vapour from the top of the tower through a condenser in which it is condensed to the liquid state.

The chief impurity in the crude bromine thus obtained is bromine chloride, $BrCl$, formed by the combination of excess of chlorine with the bromine. This is decomposed by shaking the crude product with potassium bromide, $KBr + BrCl = KCl + Br_2$; and the bromine is distilled away from the KCl.

To illustrate on a small scale the manufacture of bromine, chlorine water may be added to a solution of potassium bromide, which will at once become orange from the liberation of the bromine, $KBr + Cl = KCl + Br$. The bromine thus set free exists now diffused through a large volume of water, which cannot be separated from it in the usual way, by evaporation, because bromine is itself very volatile. An ingenious expedient is therefore resorted to, of shaking the orange liquid briskly with ether, which has a greater solvent power for bromine than is possessed by water, and therefore abstracts it from the aqueous solution: since ether does not mix to any great extent with water, it now rises to the surface of the liquid, forming a layer of a beautiful orange colour, due to the bromine which it holds in solution. This orange layer is carefully separated and shaken with solution of potash, which immediately destroys the colour by removing the bromine, leaving the ether to rise to the surface in a pure state, and fit to be employed for abstracting the bromine from a fresh portion of the water. The action of the bromine upon potash is precisely similar to that of chlorine; $6KOH + Br_6 = 5KBr + KBrO_3 + 3H_2O$.

After the solution of potash has been several times shaken with the ethereal solution of bromine, and has become highly charged with this element, it is evaporated so as to expel the water, leaving a solid residue containing the potassium bromide and bromate. This saline mass is strongly heated to decompose the bromate, and convert it into bromide; $KBrO_3 = KBr + O_3$. From this salt the bromine is extracted by distilling it with manganese dioxide and sulphuric acid, when the bromine is liberated and condensed in a receiver kept cold by iced water; $2KBr + MnO_2 + 2H_2SO_4 = K_2SO_4 + MnSO_4 + 2H_2O + Br_2$.

The aspect of bromine is totally different from that of any other element, for it distils over in the liquid condition, and preserves that form at ordinary temperatures, being the only liquid non-metallic element. Its dark red-brown colour, and the peculiar orange colour of the vapour which it exhales continually, are also characteristic; but, above all, its extraordinary and disagreeable odour, from which it derives its name (*βρῶμος, a stench*), leaves no doubt of its identity. The odour has some slight resemblance to that of chlorine, but is far more intolerable, often giving rise to great pain, and sometimes even to bleeding at the nose.

Liquid bromine is thrice as heavy as water (sp. gr. 3.18 at 0° C.), and boils at 63° C., yielding a vapour $5\frac{1}{2}$ times as heavy as air (sp. gr. 5.54).* It may be frozen at − 7° C. to a brown crystalline solid. It requires 33 times its weight of cold water to dissolve it, and forms a crystalline hydrate ($Br.5H_2O$) corresponding with chlorine hydrate.

In its bleaching power, its aptitude for direct combination, and its other chemical characters, it very closely resembles chlorine, so closely, indeed, that it is difficult to distinguish, in many cases, between the compounds of chlorine and bromine with other substances, unless the elements themselves be isolated. A necessary consequence of so great a similarity is, that very little use has been made of bromine, since the far

* At high temperatures the vapour density (sp. gr.) of bromine decreases considerably.

more abundant chlorine fulfils nearly all the purposes to which bromine might otherwise be applied. In the daguerreotype and photographic arts, however, some special applications of bromine have been discovered, and for some chemical operations, such as the determination of the illuminating hydrocarbons in coal gas, bromine is sometimes preferred to chlorine. It is applied in the manufacture of artificial dyestuffs and has also been used in America as a disinfectant. The bromides of potassium and ammonium are frequently employed in medicine. Bromide of cadmium is used in photography. Commercial bromine sometimes contains bromoform and cyanogen bromide. In the composition of their compounds chlorine and bromine exhibit great analogy, but no compound of bromine with oxygen has been obtained.

Hypobromous acid (HOBr) has been obtained in solution by shaking mercuric oxide with water and bromine. The solution is very unstable, decomposing, especially when heated, with liberation of bromine and formation of bromic acid. The action of bromine upon diluted solutions of the alkalies, and upon the alkaline earths, produces bleaching liquids similar to those formed by chlorine, and apparently containing the hypobromites of the metals.

Bromic acid ($HBrO_3$) can be prepared in a similar manner to that described for the preparation of chloric acid, to which it has a great general resemblance, the bromates being also similar to the chlorates.

118. **Hydrogen bromide** or **hydrobromic acid** (HBr = 81 parts by weight = 2 vols.)—The inferiority of bromine to chlorine in chemical energy is well exemplified in its relations to hydrogen; for the vapour of bromine mixed with hydrogen will not explode under the action of flame or of the electric spark, like the mixture of chlorine and hydrogen. Direct combination may be induced by contact with heated platinum.

When it is attempted to prepare this acid by distilling bromide of sodium or potassium with sulphuric acid (as in the preparation of hydrochloric acid) the inferior stability of hydrobromic acid is shown by the decomposition of a part of it, the hydrogen being oxidised by the sulphuric acid, and the bromine set free; $2HBr + H_2SO_4 = 2H_2O + SO_2 + Br_2$.

If a strong solution of phosphoric acid be employed instead of the sulphuric, pure hydrobromic acid may be obtained.

But the most instructive method of obtaining hydrobromic acid consists in attacking water with bromine and phosphorus simultaneously, when the phosphorus takes the oxygen of the water, forming phosphoric acid, and the bromine combines with the hydrogen to form hydrobromic acid; $3H_2O + Br_5 + P = HPO_3 + 5HBr$.

Phosphoric acid.

The experiment may be made in the apparatus shown in Fig. 156. 20 grams of red phosphorus are introduced into the flask and are covered with 40 c.c. of water. 120 grams (40 c.c.) of bromine are allowed to fall, drop by drop, from the stopcock funnel into the flask. The hydrogen bromide is passed through a U-tube containing fragments of glass mixed with moist red phosphorus, to absorb bromine, and is collected by downward displacement. After a time the flask may be gently heated.

Hydrogen bromide is very similar to hydrogen chloride; it boils at -73° C. Like that gas, it is very soluble in water, and the solution acts upon metals and their oxides in the same manner as does hydrochloric acid. Chlorine removes the hydrogen from hydrobromic acid,

liberating bromine, which it converts into *bromine chloride* if employed in excess.

Fig. 156.—Preparation of hydrobromic acid.

Nitrogen bromide has been obtained by the action of bromide of potassium upon chloride of nitrogen, which it resembles in general character and explosive properties.

Carbon tetrabromide, CBr_4, is obtained by heating CS_2 with Br at 160° C. It crystallises in white tables, melts at 91° C. and boils at 189.5° C.

Bromine chloride, BrCl, is a very volatile red-brown liquid of pungent odour. It is dissociated above 10° C. That chlorine should unite directly with bromine, which it so much resembles in chemical character, illustrates its great tendency to direct chemical combination.

IODINE.

I = 126 parts by weight.

119. Iodine is contained in sea water in even smaller quantity than bromine is, and appears to be present as *calcium iodate*, $Ca(IO_3)_2$, of which 4 parts are contained in a million of sea water,* but the iodine appears to constitute a portion of the necessary food of certain varieties of sea-weed, which extract it from the sea water, and concentrate it in their tissues. The ash remaining after sea-weed has been burnt was long used, under the name of *kelp*, in soap-making, because it contains a considerable quantity of sodium carbonate; and in the year 1811, Courtois, a soap-boiler of Paris, being engaged in the manufacture of soda from kelp, obtained from the waste liquors a substance which possessed properties different from those of any form of matter with which he was acquainted. He transferred it to a French chemist, Clement, who satisfied himself that it was really a new substance; and Gay-Lussac and Davy having examined it still more closely, it took its rank among the non-metallic elementary substances, under the name of

* The iodate may be detected in sea water by shaking with carbon disulphide and a little of the water in which phosphorus has been kept; the phosphorous acid reduces the iodate, liberating iodine, which dissolves in the CS_2 with a rose colour. It has been shown that the amount of iodine (2.3 milligrams per litre) in sea water is constant at all depths, but while it is in inorganic combination at great depths it is organically combined near the surface.

iodine (*ἰοειδής, violet-coloured*), conferred upon it in allusion to the magnificent violet colour of its vapour.

The history of the discovery of iodine affords a very instructive example of the advantage of training persons engaged in manufactures to habits of accurate observation, and, if possible, of accurate chemical observation; for had Courtois passed over this new substance as accidental, or of no consequence, the community would have lost, at least for some time, the benefits derived from the discovery of iodine.

For some years the new element was only known as a chemical curiosity, but an unexpected demand for it at length arose on the part of the physician, for it had been found that the efficacy of the ashes of sponge, which had long been used in some particular maladies, was due to the small quantity of iodine which they contained, and it was of course thought desirable to place this remedy in the hands of the medical profession in a purer form than the ash of sponge, where it is associated with very large quantities of various saline substances. Much more recently, the demand for this element has greatly increased on account of its employment in photography, and in the manufacture of artificial dyes, and large quantities of it were at one time produced from kelp.

Although the production of iodine from kelp is a dead industry, a brief description of it may be given as an excellent example of how an element may be extracted from an enormously preponderating mass of other matter. The sea-weed* is spread out to dry, and burnt in shallow pits at as low a temperature as possible; for the sodium iodide is converted into vapour and lost if the temperature is very high. The ash, which is in a half-fused state, is broken up and treated with hot water, which dissolves about half, leaving a residue consisting of calcium carbonate and sulphate, sand, &c. The whole of the sodium iodide is contained in the portion dissolved by the water, but is mixed with much larger quantities of sulphate, carbonate, hyposulphite, sulphide and bromide of sodium, together with sulphate and chloride of potassium. A portion of the water is expelled by evaporation, when the sulphate and carbonate of sodium and chloride of potassium, being far less soluble than the iodide of sodium, crystallise. In order to decompose the hyposulphite and sulphide of sodium, the liquid is mixed with an eighth of its bulk of oil of vitriol, which decomposes these salts, evolving sulphurous and hydrosulphuric acid gases, with deposition of sulphur, and forming sodium sulphate, which is deposited in crystals. The liquor thus prepared is next mixed with manganese dioxide, and heated in an iron still lined with lead (Fig. 157), when the iodine is evolved as a magnificent purple vapour, which condenses in the bottle-shaped glass or stoneware receivers (*aludels*) in the form of dark grey scales with metallic lustre, and having considerable resemblance to black lead. The liberation of the iodine is explained by the following equation—$2NaI + MnO_2 + 2H_2SO_4 = Na_2SO_4 + MnSO_4 + 2H_2O + I_2$.

Fig. 157.—Extraction of Iodine.

When no more iodine passes over, some manganese dioxide is added, and the bromine then distils. The quantity of bromine obtained is about one-tenth that of the iodine. A ton of kelp yields about 10 lbs. of iodine. The crude iodine is resublimed to purify it.

A far more economical process for the treatment of sea-weed consists in distilling

* The *Laminaria digitata*, or deep sea tangle, contains most iodine, amounting to 0.45 per cent. of the dried weed.

it, when ammonia, acetic acid, naphtha, tar, and illuminating gas are obtained, whilst a porous charcoal remains in the retort, which is treated with water in order to extract the iodides and other soluble salts. This charcoal somewhat resembles animal charcoal in character, containing much phosphate and carbonate of calcium and magnesium; it is useful as a decolorising and deodorising agent. In France the iodine is generally precipitated from the concentrated solution of kelp by passing chlorine into the solution. The precipitate is washed and resublimed.

Iodine is now imported from Chili and Peru, where it is obtained from *caliche*, the crude nitrate of soda found in certain districts of those countries. In this mineral the iodine (about 0.1 per cent.) occurs as sodium iodate ($NaIO_3$) which remains dissolved in the water from which the sodium nitrate has been recrystallised for the market. These mother liquors, containing about 22 per cent. of $NaIO_3$, are mixed with a solution containing sodium sulphite (Na_2SO_3) and sodium hydrogen sulphite ($NaHSO_3$), when the iodine is precipitated according to the equation—

$$2NaIO_3 + 3Na_2SO_3 + 2NaHSO_3 = 5Na_2SO_4 + I_2 + H_2O.$$

The precipitate is drained, pressed, and resublimed.

Besides non-volatile matter (sand and calcium sulphate), which may be eliminated by resublimation, commercial iodine is liable to contain chlorine, bromine, and cyanogen iodide. It may be freed from these volatile impurities by dissolving it in a strong solution of potassium iodide, precipitating it by the addition of water and resubliming the dried precipitate after it has been mixed with barium oxide to complete its desiccation.

The features of this element are extremely well marked: its metallic lustre and peculiar odour sufficiently distinguish it from all others, and the effect of heat upon it is very striking, in first easily fusing it (at 116° C.), and afterwards converting it (boiling-point, 183°) into the most exquisitely purple vapour, which is nearly nine times as heavy as air (sp. gr. 8.72),* and condenses upon a cool surface in shining scales. Iodine stains the skin intensely brown. The specific gravity of solid iodine is 4.95.

When iodine is shaken with cold water, a very small quantity is dissolved (about 0.05 per cent.), forming a light-brown solution. Hot water dissolves a larger quantity, but alcohol is one of the best solvents for iodine, producing a dark red-brown solution from which part of the iodine may be precipitated by adding water. A solution of potassium iodide also dissolves iodine freely (*Lugol's solution; liquor iodi*). *Tincture of iodine* contains iodine with half its weight of potassium iodide dissolved in alcohol. Benzene and carbon bisulphide dissolve it abundantly, producing fine violet-red solutions, which deposit the iodine, if allowed to evaporate spontaneously, in minute rhombic octahedral crystals aggregated into very beautiful fern-like forms. If an extremely weak aqueous solution of iodine be shaken with a little carbon bisulphide, the latter will remove the iodine from the solution, and, on standing, will fall to the bottom of the liquid, having a beautiful rose colour. By dissolving a large quantity of iodine in carbon bisulphide, a solution is obtained which is perfectly opaque to rays of light, though it allows heat rays to pass freely, and is therefore of great value in physical experiments. A solution of iodine in carbon tetrachloride is also used for the same purpose.

* The vapour density of iodine vapour falls with rise of temperature.

Existing, as iodine does, in very minute quantity in the water from various natural sources, it would often be overlooked if the chemical analyst did not happen to possess a test of the most delicate description for it. Iodine, in the uncombined state, dyes starch of a beautiful blue colour, as may be proved by heating a grain or two of the element with water, and adding to the cold solution a little thin starch, or by placing a minute fragment of iodine in a stoppered bottle, and suspending in it a piece of paper dipped in thin starch. This test, however, though sensitive to the smallest quantity of free iodine, gives no indication whatever with iodine in combination, as it always exists in nature; in order, therefore, to test for iodine, a little starch-paste is added to the suspected liquid, and then a drop of a weak solution of chlorine, which will set free the iodine, and cause the production of the blue colour. It is necessary, however, carefully to avoid adding too much chlorine, since it would immediately destroy the colour of the iodised starch: if this has been done, a very little sulphurous acid will bring back the blue tint, which will be again bleached by more sulphurous acid.* Alkalies also bleach it, and the colour of a mixture of the iodised starch with water is removed by heating, but returns in great measure when the solution cools. The starch appears to be only dyed by the iodine, and not combined with it; on shaking the blue iodised starch for some time with CS_2, the blue colour is removed, and the red solution of iodine in CS_2 is obtained.

This delicate test for iodine has enabled the chemist to show that the element is widely distributed in very small quantities. It has been found in the floating matter of the air, in various fungi, in forest trees, and in the animal body, particularly the thyroid gland.

Though very closely connected with chlorine and bromine in its general chemical relations, there are several points in the history of iodine which cause it to stand out in marked contrast by the side of these elements. The attraction which binds it to hydrogen and the metals is certainly weaker than that exerted by chlorine and bromine, so that either of these is capable of displacing it from its compounds, and its bleaching properties are very feeble. Cl, uniting with H, produces 22,000 heat-units; gaseous Br produces 12,100, but gaseous I produces practically no thermal effect.† Hence HI is much less stable than HBr or HCl. On the other hand, iodine exhibits a more powerful tendency to unite with oxygen; for boiling nitric acid converts it into iodic acid (HIO_3), though this oxidising agent would not affect chlorine or bromine. Iodine is also capable of direct oxidation by ozone.

Iodine pentoxide, I_2O_5, is the only oxide of iodine which is known with certainty; it is the anhydride of iodic acid ($H_2O.I_2O_5 = 2HIO_3$), and is a white crystalline substance obtained by heating the acid. The product of the oxidation of iodine by ozone is a yellow deliquescent powder (formerly supposed to be I_2O_3), the exact composition of which has not been elucidated,

Evidence has been obtained, from the existence of certain organic compounds, that iodine is able to form a base on the type of ammonia. When this base is isolated it will probably have the formula $IH_2(OH)$, being the analogue of hydroxylamine $NH_2(OH)$.

Some of the compounds of iodine with the metals are remarkable for their

* The following equations explain these changes:
(1) $KI + Cl = KCl + I$; (2) $I + 3H_2O + Cl_5 = HIO_3 + 5HCl$;
(3) $2HIO_3 + H_2SO_3 = 5H_2SO_4 + I_2 + H_2O$; (4) $I_2 + H_2O + H_2SO_3 = 2HI + H_2SO_4$.

† The formation of HI from H and solid I *absorbs* 6000 heat-units.

beautiful colours. The *mercuric iodide*, produced by mixing solutions of potassium iodide and mercuric chloride, forms a fine scarlet precipitate, which dissolves in an excess of potassium iodide to a *colourless* solution.

Lead iodide has a bright yellow colour, as may be seen by precipitating potassium iodide with a solution of lead acetate. The precipitate is dissolved by boiling with water (especially on adding a little hydrochloric acid), forming a colourless solution, from which the lead iodide crystallises in very brilliant golden scales on cooling. *Silver iodide* is produced as a yellow precipitate when silver nitrate is added to potassium iodide. The bromide and chloride of silver would form white precipitates. Silver iodide is more stable than the chloride or bromide; when exposed to light it appears to be unchanged, but if a reducing agent, such as ferrous sulphate or pyrogallin, be afterwards poured over it, that portion of the iodide which has been exposed to light is immediately blackened, from the separation of silver in the metallic state. This is the principle of the process for developing the negative photograph taken on a collodion film rendered sensitive by silver iodide. The iodides of potassium, ammonium, and cadmium are also used in photography.

120. **Iodic acid, HIO_3 or $IO_2(OH)$,** is most easily prepared by boiling iodine with the strongest nitric acid in a long-necked flask, when it is dissolved in the form of iodic acid, which is left, on evaporating the nitric acid, as a white mass. This may be purified by dissolving in water and crystallising, when the iodic acid forms white hexagonal tables. Heated to 180° C. the iodic acid is decomposed into water and iodic anhydride, $2HIO_3 = H_2O + I_2O_5$. This last is decomposed at about 370° C. into iodine and oxygen. The iodic anhydride oxidises combustible bodies, but not with any great violence. The acid is far more stable than chloric or bromic acid. Its solution first reddens litmus-paper, and afterwards bleaches it by oxidation. Its salts, the *iodates*, are less easy soluble in water than are the chlorates and bromates, which they resemble in their oxidising action upon combustible bodies. They are all decomposed by heat, evolving oxygen, and sometimes even iodine, showing how much inferior this element is to chlorine and bromine in its attraction for metals.

Potassium iodide may be oxidised directly to potassium iodate, KIO_3, by potassium permanganate. Iodic acid forms acid potassium salts of the formulæ KHI_2O_6 and $KH_2I_3O_9$, the existence of which, together with the fact that the acid readily yields an anhydride and water when heated (an uncommon reaction for a monobasic acid), and with other evidence, indicates that the acid is di- or even tri-basic.

Periodates.—The periodates (such as $AgIO_4$), analogous to the perchlorates, are known, but the simple acid HIO_4 has not been isolated. The *periodic acid*, H_5IO_6 or $IO(OH)_5$, is prepared as follows: Chlorine is passed through a solution of sodium iodate containing NaOH, whereupon the salt $IO(OH)_3(ONa)_2$ crystallises from the solution; $NaIO_3 + 3NaOH + Cl_2 = 2NaCl + IO(OH)_3(ONa)_2$. This sodium salt is dissolved in HNO_3 and $AgNO_3$ is added; a brown precipitate of Ag_2HIO_5 is obtained. When this is dissolved in HNO_3 and the solution is evaporated red crystals of $AgIO_4.H_2O$ separate, and by treating these with water H_5IO_6 passes into solution, whilst $Ag_4I_2O_9.3H_2O$ remains undissolved. Periodic acid crystallises from this solution in colourless prisms; it decomposes when heated, yielding H_2O, O and I_2O_5. A solution of the acid is a powerful oxidant.

The periodates are referable to four types, termed respectively, the *meta-salts*, from the acid HIO_4 or $IO_3(OH)$; the *meso-salts*, from the acid H_3IO_5 or $IO_2(OH)_3$; the *para-salts*, from the acid H_5IO_6 or $IO(OH)_5$; and the *dimeso-salts*, from the acid $H_4I_2O_9$ or $2IO_2(OH)_3 - H_2O$. It thus happens that a large number of these salts are known; they are sparingly soluble.

When iodine is dissolved in an alkali an iodide and an iodate are formed; $6NaOH + I_6 = 5NaI + NaIO_3 + 3HOH$. In the case of chlorine and bromine the analogous reaction yields a hypochlorite and a hypobromite respectively; but the evidence for the existence of a hypoiodite

in the alkaline solution of iodine is very feeble. When such an alkaline solution of iodine is acidified, all the iodine is liberated, for the hydriodic acid and the iodic acid set free immediately react, the iodic acid oxidising the hydriodic acid; $HIO_3 + 5HI = 3HOH + I_6$.

121. **Hydrogen iodide or hydriodic acid** (HI = 128 parts by weight = 2 vols.).—Iodine vapour combines with hydrogen at 450° C. to form hydrogen iodide. The gas is best prepared by decomposing water with iodine in the presence of phosphorus; $P + I_5 + 4HOH = PO(OH)_3 + 5HI$ or, if a smaller proportion of iodine be used $PI_3 + 3HOH = P(OH)_3 + 3HI$.

6.5 grams of potassium iodide are dissolved in 3 c.c. of water in a retort (Fig. 158), and 13 grams of iodine are added; when this has dissolved, 0.65 gram of red phosphorus are introduced, and the mixture heated very gradually, the gas being collected by downward displacement in stoppered bottles, which must be placed in readiness, as the gas comes off very rapidly. These quantities will fill four pint bottles with the gas.

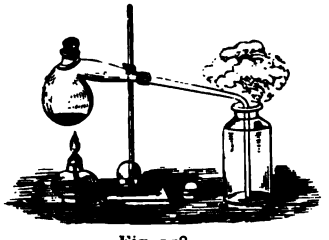


Fig. 158.
Preparation of hydriodic acid.

Hydrogen iodide is very similar in its properties to hydrogen chloride and bromide, fuming strongly in moist air, very readily absorbed by water, liquefied only under strong pressure, and solidified by extreme cold. It is much heavier, its specific gravity being 4.44. If a bottle of hydriodic acid gas be placed in contact with a bottle containing chlorine or bromine vapour diluted with air (Fig. 69) the HI will be instantly decomposed, with separation of the beautiful violet vapour of iodine. The gas is decomposed by light at the ordinary temperature and is dissociated when heated.*

The aqueous solution of hydriodic acid is most conveniently prepared by passing hydrosulphuric acid gas through water in which iodine is suspended, $H_2S + I_2 = 2HI + S$, the separated sulphur being filtered off, and the solution boiled to expel the excess of hydrosulphuric acid. By this method it is not possible to obtain a solution of HI of greater sp. gr. than 1.56 (50 per cent. HI; the strongest solution has a sp. gr. of 1.99), for a strong solution of hydriodic acid converts sulphur into H_2S.

The iodine is only able to decompose the H_2S by virtue of the fact that the HI produced has an affinity for the water; since this affinity diminishes as the liquid grows stronger, a period is soon reached when the dissolution of the HI in the water can no longer supply enough energy to enable the iodine to decompose the H_2S. In other words, the reaction only occurs so long as it is exothermic, which will be the case until the heat produced by the dissolution of the HI in water is equal to that absorbed in the decomposition of the H_2S by the iodine.

Solution of hydriodic acid differs greatly from hydrochloric and hydrobromic acids, in being decomposed by exposure to air, particularly in light, its hydrogen being oxidised and iodine separated, which dissolves in the liquid, and renders it brown.

This tendency of the hydrogen of hydriodic acid to combine with

* At 350° C. 17.3 per cent., at 394° C. 19.5 per cent., and at 448° C. 21.5 per cent. of the gas is dissociated.

oxygen renders that acid a powerful *reducing* agent. It is even capable of reducing sulphuric acid to hydrosulphuric acid—

$$H_2SO_4 + 8HI = H_2S + 4H_2O + I_8$$

so that when potassium iodide is heated with concentrated sulphuric acid, hydrosulphuric acid is evolved in considerable quantity. It will be remembered that HCl does not reduce H_2SO_4, whilst HBr only reduces it to H_2SO_3.

The action of hydriodic acid upon the metals and their oxides is generally similar to that of the other hydrogen acids. In organic chemistry, hydriodic acid is often employed for introducing hydrogen into a compound; thus, by heating benzene with hydriodic acid it may be made to take up 6 atoms of hydrogen; $C_6H_6 + 6HI = C_6H_{12} + I_6$. Since the attraction of iodine for hydrogen is so feeble, metalepsis does not occur between this halogen and hydrocarbons.

The circumstance that the organic compounds containing iodine are generally much less volatile, and therefore more manageable, than those of chlorine and bromine, leads to the extensive employment of this element in researches upon organic substances.

When potassium is heated in a measured volume of gaseous hydriodic acid, the iodine is removed, and the hydrogen occupies half the original volume. Hence 1 volume of hydrogen is combined with 1 volume of iodine vapour in 2 volumes of hydriodic acid.

122. Compounds of *carbon* with iodine, analogous in composition to the chlorine compounds of this element, are known. They are solids, it being generally the case that iodine compounds are less volatile than the corresponding chlorine compounds.

Nitrogen iodide.—The action of chlorine, bromine, and iodine upon ammonia exemplifies the difference in their attraction for hydrogen; for whilst chlorine and bromine, acting upon ammonia, cause the liberation of a certain amount of nitrogen, iodine simply removes part of the hydrogen, and itself fills up the vacancies thus occasioned, no nitrogen being liberated, the hydriodic acid thus formed combining with more ammonia to form ammonium iodide. Nitrogen iodide, NI_3, is formed at the same time.

It appears that when iodine is dissolved in dilute ammonia NH_4I and *hypoiodous acid* are formed; $NH_3 + I_2 + H_2O = NH_4I + HOI$. The hypoiodous acid then reacts with more ammonia to form nitrogen iodide; $NH_3 + 3HOI = NI_3 + 3H_2O$.

By another theory the nitrogen iodide, alleged to have the formula $N_2H_3I_3$, is formed as a decomposition product of ammonium hypoiodite; $3NH_4OI = N_2H_3I_3 + NH_3 + 2H_2O$. The hypoiodite would be formed when the iodine dissolved in excess of ammonia; $I_2 + 2NH_3 + H_2O = NH_4I + NH_4OI$.

To prepare the iodide of nitrogen 1.3 gram of iodine is rubbed to powder in a mortar and mixed with 14 c.c. of strong ammonia: the mortar is covered with a glass plate, and after about half an hour the iodide of nitrogen is collected in separate portions upon four filters, which are allowed to drain and spread out to dry. The brown solution contains iodine dissolved in ammonium iodide.

Another method consists in dissolving iodine in a mixture of hydrochloric with a little nitric acid, with the aid of heat, and adding ammonia, which decomposes the ICl in solution, and gives a black precipitate of the iodide of nitrogen.

When dry NH_3 gas is passed over iodine the two combine, several compounds, such as $(NH_2)_2I$, being formed.

The iodide is a black powder, which explodes with a loud report even when touched with a feather, the violence of the explosion being accounted for by the sudden evolution of a large volume of gas and

vapour from a small volume of solid. Even when allowed to fall from the height of a few feet upon the surface of water, it explodes if perfectly dry. In the moist state it slowly undergoes decomposition.

123. Iodine forms two compounds with chlorine, *monochloride* (ICl) and *trichloride* (ICl_3). The former is obtained by passing dry chlorine over dry iodine until it becomes a red-brown liquid. This solidifies when cooled and then melts at 14° C., but is unstable, readily passing to another form which melts at 27° C.

The trichloride forms fine red needle-like crystals, and is produced when iodine or hydriodic acid gas is acted upon with an excess of chlorine. It is useful as a germicide. The chlorides of iodine are decomposed by water, yielding HIO_3, HCl, and iodine. From the aqueous solution of ICl, ether extracts a yellow volatile compound having the composition ICl.HCl.

Iodine bromide, IBr, is a crystalline solid resembling iodine, fusing at 36° C. and subliming with partial decomposition. Water decomposes it, iodine being separated.

FLUORINE.

F = 19 parts by weight.

124. The most ornamental mineral substance occurring in any abundance in this country is known as *fluor spar*, *Derbyshire spar*, or *blue John* (fluoride of calcium), and is found with several beautiful shades of colour—blue, purple, violet, or green, and sometimes perfectly colourless, either in large masses or in crystals, which have the form of a cube or of some solid derived from it. The use of this mineral as a flux in smelting ores dates from a very remote period, and from this use the name fluor appears to have been originally derived; but we have no record of its chemical examination until 1764, when Margraf found his glass retort powerfully corroded in distilling this mineral with sulphuric acid, and Scheele soon after announced that it contained lime and *fluoric acid*. But though this chemist had fallen into the error to which analysts are continually liable, of mistaking products for educts, his experiments, as they were afterwards perfected by Gay-Lussac and Thénard, deserve particular consideration.

125. **Hydrogen fluoride** (HF = 20 parts by weight = 2 volumes).*—If powdered fluor spar be mixed with twice its weight of oil of vitriol, and heated in a leaden retort (Fig. 159), the neck of which fits tightly into a leaden condensing-tube, cooled in a mixture of ice and salt, a colourless liquid distils over, and the residue in the retort is found to consist of calcium sulphate;† $CaF_2 + H_2SO_4 = CaSO_4 + 2HF$. The colourless liquid (hydrofluoric acid) possesses most remarkable properties; it is powerfully acid, fumes strongly in the air, and has a most pungent irritating odour. If the air is at all warm, the liquid begins to boil when taken out of the freezing-mixture. Should the operator have the misfortune to allow a

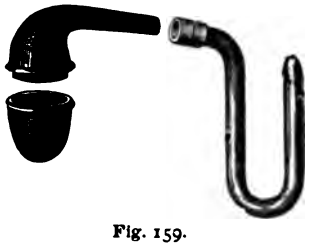


Fig. 159.

* The vapour density of hydrogen fluoride is 25.6 at 26.4° C., and gradually diminishes until the temperature reaches 89° C., when it remains constant at 10; this shows that at temperatures below 89° C. the molecule of this gas is more complex than is represented by the formula HF, but becomes HF at 89° C.

† The mineral kryolite (fluoride of aluminium and sodium) may be advantageously substituted for fluor spar, being more easily obtained in a pure state.

drop to fall upon his hand, it will produce a very painful sore, even its vapour producing pain under the finger nails. Its attraction for water is so great, that the acid hisses like red-hot iron when brought in contact with water. But its most surprising property is that of rapidly corroding glass, which has already been alluded to as noticed by Margraf. Experiment soon proved that great analogy existed between the properties of this new acid and those of hydrochloric acid; and Ampère was led to believe that the acid was a hydrogen acid, containing a new salt radicle, which he named fluorine; the name of the acid was then changed from fluoric to hydrofluoric acid.

This liquid has since been proved to be a solution of hydrofluoric acid in water; for if it be distilled with phosphoric anhydride, which retains the water, it evolves hydrofluoric acid gas, which resembles hydrochloric acid gas in fuming strongly on contact with moist air and being eagerly absorbed by water, but has a far more pungent odour.

Pure hydrogen fluoride is prepared by heating dry *potassium hydrogen fluoride* (KHF_2) to redness in a platinum still. It is then obtained as a colourless liquid, which boils at 19° C., and has the specific gravity 0.985 at 12° C. It solidifies at −102° C. and melts again at −92°. The pure acid scarcely affects metals, excepting potassium and sodium. It corrodes glass, however, rapidly, though its vapour has little action on glass unless moisture be present. It combines eagerly with sulphuric and phosphoric anhydrides, with great evolution of heat, a circumstance in which it resembles water, and differs altogether from its more obvious analogue, hydrochloric acid. It is also found that it combines energetically with the fluorides of potassium and sodium, precisely as water combines with the oxides of those metals.

It is remarkable that the solution of hydrofluoric acid, in its concentrated form, is not so heavy as a somewhat weaker acid. Thus the acid of sp. gr. 1.06 acquires the sp. gr. 1.15 on addition of a little water; but on adding more water, its sp. gr. is again reduced. It would hence appear that the acid of 1.15 is a definite hydrate of hydrofluoric acid; its composition corresponds with $HF.2H_2O$. It distils unchanged at 248° F. (120° C.).

The solution of hydrofluoric acid is generally kept in bottles made of gutta-percha. Its action on metals and their oxides resembles that of hydrochloric acid. It dissolves all ordinary metals except gold, platinum, silver, mercury, and lead. Strange to say, it has but little action on magnesium.

The property which renders this acid so useful to the chemist is its power of dissolving silica even in its most refractory form. When sand or flint reduced to powder is digested in a leaden or platinum vessel with hydrofluoric acid, it is gradually dissolved; and if the solution be evaporated, the whole of the silica will be found to have disappeared in the form of gaseous silicon tetrafluoride; $SiO_2 + 4HF = SiF_4 + 2H_2O$. If the silica be combined with a base, the metal will be left as a fluoride decomposable by sulphuric or hydrochloric acid. This renders hydrofluoric acid a most valuable agent in the analysis of the numerous mineral silicates which resist the action of other acids.

The corrosion of glass by hydrofluoric acid is now easily explained. Ordinary glass consists of silicate of sodium or potassium combined with

ilicate of calcium or lead. The hydrofluoric acid attacks and remov he silica, and thus eats its way into the glass.

In order to demonstrate the action of this acid upon glass, a glass plate warmed sufficiently to melt wax, a piece of which is then rubbed over it, until t glass is covered with a thin and pretty uniform coating. Upon this a word drawing may be engraved with a sharp point so that the lines shall expose t glass. The glass plate is then placed, wax downwards, over a leaden or platinu dish containing a mixture of fluor spar and strong sulphuric acid, exposed to very gentle heat, and allowed to remain for a quarter of an hour; the plate then gently warmed to melt the wax, which may be wiped off with a little to when it will be found that the hydrofluoric acid evolved from the mixture h corroded those portions of the glass from which the graver had removed t wax. This process is applied to the marking of glass instruments.

The solution of hydrofluoric acid etches glass without deadening the surface, is the case with the vapour; but a solution of fluoride of potassium or ammoniu mixed with sulphuric acid does produce a dead surface, and is much used f engraving on glass. An ink sold for writing on glass with a steel pen is compos of barium and ammonium fluorides and sulphuric acid.

126. When hydrofluoric acid was first obtained it was soon evide that it was not an element, because it yielded hydrogen when treat with metals, and its analogy to hydrochloric acid led naturally to th assumption that it was a compound of hydrogen with only one oth element, which was called fluorine. All attempts to isolate this elemen however, failed, owing to the great attraction which it possesses f other elements. It was not until Moissan, in 1886, prepared very pu hydrogen fluoride, and discovered that an alloy of platinum with 10 p cent. of iridium wou withstand the attack fluorine, that he su ceeded in electrolysi HF with liberation fluorine at the anod quantity sufficient the properties of element to be exam

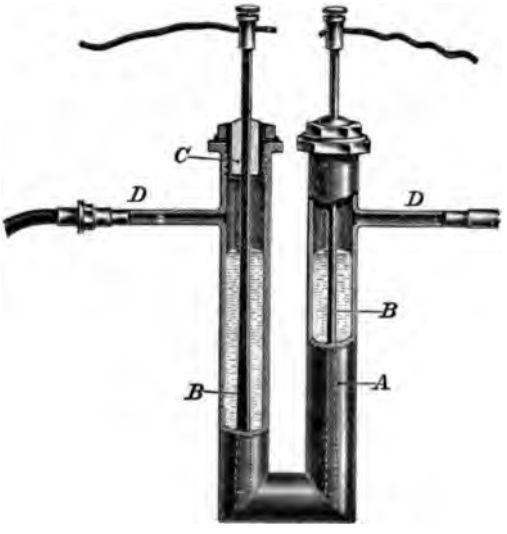


Fig. 160.—Isolation of fluorine.

Fig. 160 illustrate electrolytic cell us Moissan. The U-tub made of the aforesaid as also are the electr passing through sto made of fluor spar insulates them fr metal of the U-tu cell contains pur hydrogen fluoride about 20 per cent sium fluoride diss and is immersed methyl chloride is cooled to – 23 rent from 25 B is passed throug

The liberated gases escape by the side tube *D*, the hydrogen being se negative electrode and the fluorine at the positive electrode. To free from the HF it is passed over dry KF.

Fluorine is a greenish-yellow gas, which becomes liquid

and has the properties of chlorine, but much more strongly marked. It decomposes water immediately, seizing upon its hydrogen and liberating oxygen in the ozonised condition; it explodes with hydrogen even in the dark,* and nearly all non-metals and many metals take fire in it at ordinary temperatures.

Some metals, however, become coated with fluoride and need to be heated before they burn in the gas. Gold and platinum resist attack at temperatures below 300° C., and carbon is fairly resistant unless finely divided. Oxygen, nitrogen, chlorine, and argon appear to be unattacked by fluorine; hydrogen chloride explodes with it, yielding HF and Cl.

Fluorine can also be obtained by heating the tetrafluorides of certain metals (just as chlorine is evolved from their tetrachlorides). By this method the element has been prepared from the tetrafluorides of lead and of cerium. The great activity of the gas has rendered a detailed study of its properties difficult; it appears, however, that its vapour density is slightly lower than 19, indicating that the gas contains free atoms, as well as molecules of F_2, at the ordinary temperature. This may account for its activity.

Fluorides.—Solutions of the fluorides of potassium and the other alkali metals corrode glass slowly, like hydrofluoric acid. The fluorides are capable of combining with the acid; thus potassium fluoride forms KF.HF, which, when dry, is a convenient source of HF gas when moderately heated. The only fluoride possessed of much practical interest, beside the fluoride of calcium, is the mineral *kryolite* (*χρύος, frost*), which is a double fluoride of aluminium and sodium (Na_3AlF_6), found abundantly in Greenland, and valuable as a source of aluminium.

The *topaz* contains fluorine, but in what form of combination is not certain; its other constituents are alumina and silica. *Tourmaline* also contains fluorine, together with alumina, silica, and FeO. In such minerals it is probable that the F is substituted for part of the O.

Magnesium fluoride (MgF_2) forms the mineral *Sellaite* which is found, crystallised, in Savoy. Fluorides are also found, though in very small quantity, in sea water, and they have been discovered in plants and animals. Human bone contains about 2 per cent. of calcium fluoride.

No compound of fluorine with oxygen is known.

Carbon tetrafluoride, CF_4, is a colourless gas made by burning lamp black in fluorine; it boils at −15° C. and is said to be produced in quantity, when kryolite is electrolysed for winning aluminium (*q.v.*).

127. **General review of chlorine, bromine, iodine, and fluorine.**—These four elements compose a natural group, the members of which are connected by the similarity of their chemical properties far more closely than those of any other group of elements. They are usually styled the *halogens*, from their tendency to produce salts resembling sea salt in their composition (*ἅλς, the sea*), and such salts are called *haloid salts*. These elements are also called *salt-radicles*, from their property of forming salts by direct union with the metals. Each is monatomic, and combines with an equal volume of hydrogen to form an acid which occupies the joint volumes of its constituents.

The halogens also supply the most prominent example of the gradation in properties observed among the members of the same natural group of elements.

In the order of their chemical energy, that is, of the force with which

* Evolving 39,000 calories per 20 grams of HF formed.

they hold other elements in chemical combination with them, fluorine should stand first, its combining energy being so great as to cause a serious difficulty in isolating it; chlorine would rank next, then bromine, and iodine last.

The atomic weights follow the inverse order of their chemical energies: fluorine, 19; chlorine, 35.5; bromine, 80; iodine, 127—numbers which, of course, also represent their relative specific gravities in the state of vapour.

A similar gradation is observed in their physical state and colour, fluorine being a yellow gas, chlorine a yellow gas, bromine a red liquid boiling at 63° C., and iodine a black solid boiling at 183° C.

Even in the exceptions which occur to the order of chemical energy above alluded to, the same progression is noticed: thus fluorine has so little attraction for oxygen that no oxide is known; chlorine has less attraction for oxygen than bromine (chloric acid being less stable than bromic); whilst bromine has less than iodine, which is capable even of uniting directly with ozonised oxygen.

The compounds of these elements with hydrogen are all gases distinguished by a powerful attraction for moisture and great similarity of odour. Their potassium salts all crystallise in the same (cubical) form.

The silver fluoride is deliquescent and soluble in water; the chloride is insoluble in water, but dissolves very easily in ammonia; the bromide dissolves with some difficulty in ammonia; and the iodide is insoluble, In some other particulars, fluorine stands apart from the other halogens; thus, the fluoride of calcium is a very insoluble substance, whilst the chloride, bromide, and iodide are very soluble. Hydrofluoric acid forms KHF_2, which corresponds in composition with KHO.

It is noteworthy that these halogen elements are *par excellence* acid elements; that is to say, not only their oxygen compounds but their hydrogen compounds exhibit acid properties. The carbon family gives neutral hydrogen compounds; the nitrogen family gives basic hydrogen compounds, whilst the sulphur family gives feebly acid hydrogen compounds.

SULPHUR.

S = 32 parts by weight = 1 volume (at 1000° C.).

128. Sulphur is remarkable for its abundant occurrence in nature in the uncombined state in many volcanic districts. It is also found, as sulphuretted hydrogen, in many mineral waters, and very abundantly in combination with metals, forming the numerous ores known as *sulphurets* or *sulphides*, of which the following are the most abundant:

Iron pyrites,	Iron disulphide,	FeS_2
Copper pyrites,	Sulphide of iron and copper,	$Cu_2S.Fe_2S_3$
Galena,	Sulphide of lead,	PbS
Blende,	Sulphide of zinc,	ZnS
Crude antimony,	Sulphide of antimony,	Sb_2S_3
Cinnabar,	Sulphide of mercury,	HgS.

Sulphur is plentifully distributed also, in combination with oxygen and a metal, in the form of *sulphates*, of which the most conspicuous are

Gypsum,	Sulphate of calcium,	$CaSO_4.2H_2O$
Heavy spar,	Sulphate of barium,	$BaSO_4$
Celestine,	Sulphate of strontium,	$SrSO_4$
Epsom salts,	Sulphate of magnesium,	$MgSO_4.7H_2O$
Glauber's salt,	Sulphate of sodium,	$Na_2SO_4.10H_2O$.

In plants, sulphur is also found in the form of sulphates, and as a constituent of the vegetable albumin (of which it forms about 1.5 per cent.) present in the sap. It is also contained in certain of the essential oils remarkable for their peculiar pungent odour, such as those of garlic and mustard.

In animals, sulphur occurs as sulphates, as a constituent of albumin, fibrin, and casein (in none of which does it exceed 2 per cent.), and in bile, one of the products from which, taurine, contains 25 per cent. of sulphur.

For our supplies of sulphur we are chiefly indebted to Sicily, where large quantities of it are found in an uncombined state in beds of blue clay. Magnificent crystalline masses of strontium sulphate are often found associated with it; the sulphur itself sometimes occurs in the form of transparent yellow octahedra, but more frequently in opaque,

Fig. 161.—Distillation of sulphur.

amorphous masses. The districts in which sulphur is found are usually volcanic, and those which border the Mediterranean are particularly rich in it. Sulphur has also been found in Iceland and New Zealand.

The *native* sulphur, being commonly distributed in veins through masses of gypsum and celestine, has to be separated from these by the action of heat. When the ores contain more than 12 per cent. of sulphur, the bulk of it is melted out, the ore being thrown into rough furnaces or cauldrons with a little fuel, and smothered up with earth, so as to prevent the combustion of the sulphur, which runs down in the liquid state to the bottom of the cauldron, and is drawn out into wooden moulds.* But when the proportion of sulphur is small, the ore is heated so as to convert the sulphur into vapour, which is condensed in another vessel. The operation is conducted in rows of earthen jars (A, Fig. 161) heated in a long furnace, and provided with short lateral

* High pressure steam has been applied with advantage for melting the sulphur out of the ores, which are enclosed in an iron vessel; or the ores are heated in a boiler with a 66 per cent. solution of calcium chloride at 120° C. The sulphur is sometimes extracted by dissolving it with carbon bisulphide. When sulphur ores containing calcium sulphate are distilled, part of the sulphur is lost as sulphur dioxide, which goes off as gas—

$$CaSO_4 + S_2 = CaS + 2SO_2.$$

pipes, which convey the sulphur into similar jars (B) standing outside the furnace, in which the vapour of sulphur condenses in the liquid state, and flows out into pails of water. The sulphur obtained by this process is imported as *rough sulphur*, and contains 3 or 4 per cent. of earthy impurities. In order to separate these, it is redistilled, in this country, in an iron retort (A, Fig. 162), from which the vapour is conducted into a large brick chamber (B), upon the sides of which it is

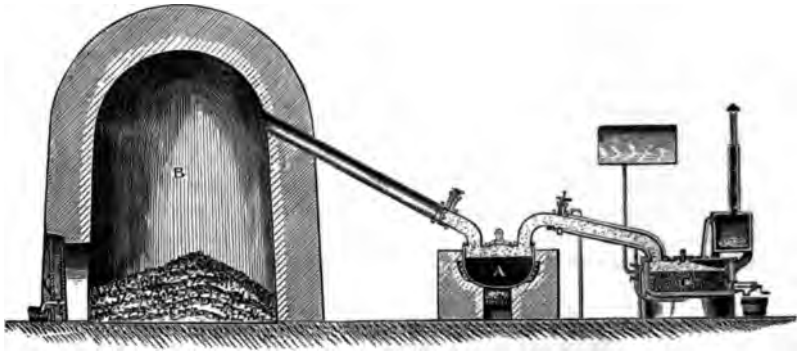


Fig. 162.—Sulphur refinery.

deposited in the form of a pale yellow powder (*flowers of sulphur*, or *sublimed sulphur*). When the operation has been continued for some time, the walls of the chamber become sufficiently hot to melt the sulphur, which is allowed to collect, and afterwards cast in wooden moulds, forming *roll sulphur* or *brimstone*. *Distilled sulphur* is obtained by allowing the vapour to pass from the retort into a small receiving vessel (C) cooled by water, where it condenses in the liquid state; this variety of sulphur is preferred for the manufacture of gunpowder, for reasons which will be stated hereafter.

Sulphur is readily distilled on a small scale in a Florence flask (Fig. 163), another flask cut off at the neck being employed as a receiver. The flask containing the sulphur should be supported upon a thin iron wire triangle, and heated by a gauze burner, at first gently, and afterwards to the full heat. Flowers of sulphur will at first condense in the receiver, and will be followed by distilled sulphur when the temperature increases. A slight explosion of the mixture of sulphur vapour and air may occur at the commencement of the distillation. An ounce of sulphur may be distilled in a few minutes.

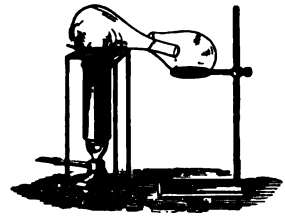


Fig. 163.—Distillation of sulphur.

We are by no means entirely dependent upon Sicily for sulphur, for this element can be easily extracted from iron and copper pyrites, both of which are found abundantly in this country.

Iron pyrites forms the yellow metallic-looking substance which is often met with in masses of coal, sometimes in distinct cubical crystals, and is to be picked up in large quantities on some sea-beaches, where it occurs in rounded nodules, rusty outside, but having a fine radiated metallic fracture. When this mineral is strongly heated, it gives up part of its sulphur; at a very high temperature one-half of the sulphur

may be separated, $FeS_2 = FeS + S$, but by an ordinary furnace heat only about one-fourth can be obtained. The distillation of iron pyrites is sometimes effected in conical fireclay retorts, but it is not now much practised. The sulphur obtained in this way has a green colour, due to the presence of a little sulphide of iron carried over mechanically during the distillation: in order to purify it, it is melted and allowed to cool slowly, when the sulphide of iron subsides; the upper portion of the mass is then further purified by distillation.

Sulphur may also be obtained from copper pyrites ($Cu_2S.Fe_2S_3$) in the process of roasting the ore, previously to the extraction of the copper. The ore is heaped up into a pyramid, the base of which is about 30 feet square: a layer of powdered ore is placed at the bottom, to prevent too rapid access of air: above this there is a layer of brushwood: a wooden chimney is placed in the centre, and is made to communicate with air-passages left between the faggots: around this chimney the large fragments of the ore are piled to a height of about 8 feet, and a layer of powdered ore, about 12 inches deep, is strewn over the whole. The heap contains about 2000 tons of pyrites, and will yield 20 tons of sulphur. The fire, being kindled by dropping lighted faggots down the chimney, burns very slowly, because of the limited access of air, and after a few days sulphur is seen to exude from the surface, and is received in cavities made for the purpose in different parts of the heap. The roasting requires five or six months for its completion. In this operation a part of the sulphur has been separated by the mere action of heat, and another part has been displaced by the oxygen of the air, which has converted a portion of the iron into an oxide. A part of the separated sulphur has been burnt, the rest having escaped combustion on account of the limited access of air. The sulphur extracted from pyrites is generally found to contain a little arsenic, which is frequently associated with minerals.

Much sulphur is now prepared from the sulphuretted hydrogen from the *tank-waste* of the alkali works, and from the ammoniacal liquor of gas works, by a process which will be described under the manufacture of carbonate of soda.

Immense quantities of sulphur are consumed in this country for the manufacture of sulphuric acid, gunpowder, lucifer matches, vulcanised caoutchouc, and for making the sulphurous acid gas employed in bleaching processes.

129. *Properties of sulphur.*—In its ordinary forms sulphur has a characteristic yellow colour, though *milk of sulphur*, or precipitated sulphur (obtained by adding an acid to the solution of sulphur in an alkali), is white. It suffers electrical disturbance with remarkable facility, so that when powdered in a dry mortar it clings to the mortar with great pertinacity.

Finely divided sulphur, especially sublimed sulphur, is gradually oxidised and converted into sulphuric acid when exposed to moist air.

One of the most remarkable features of sulphur is its inflammability, due to its tendency to combine with oxygen at a moderately elevated temperature. It melts at 115° C. (239° F.), and inflames at about 260° C. (500° F.), burning with a pale blue flame and emitting the well-known suffocating odour of sulphurous acid gas (SO_2). The changes in the physical condition of this element under the influence of heat are very extraordinary. If a quantity of sulphur be introduced into a Florence flask and subjected to a gradually increasing heat (Fig. 164), it is soon converted into a pale yellow limpid liquid (120° C.), the colour of which becomes gradually brown as the temperature rises, until, at about 200° C., it is nearly black and opaque, and is so viscid that the

flask may be inverted without spilling it: at this point the temperature of the sulphur remains stationary for a time, notwithstanding that it is still over the flame, showing that heat is becoming latent in converting the sulphur into the new modification. On continuing the heat the sulphur once more becomes liquid, though not so mobile as at first, and at a much higher temperature, 440° C. (836° F.), it boils, and is converted into a brownish red, very heavy vapour: at this point of the experiment an explosion of the mixture of sulphur vapour with air often occurs. The flask may now be removed from the flame, and a little of the sulphur poured into a vessel of water, through which it will descend in a continuous stream, forming a soft elastic string like india-rubber: the portion remaining in the flask will be observed, as it cools, to pass again through the same states, becoming viscid at 200° C., and very liquid at 120° C.; another portion may now be poured into water, through which it will fall in isolated drops, solidifying into yellow brittle crystalline buttons of ordinary sulphur. As the portion of sulphur left in the flask cools, it will be found to deposit small tufts of crystals, and ultimately to solidify altogether to a yellow crystalline mass.

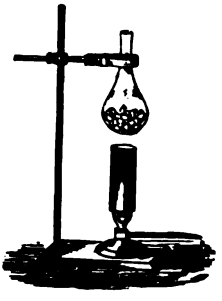


Fig. 164.

The brown *ductile sulphur*, when kept for a few hours, will become yellow and brittle, passing, in great measure, spontaneously into the crystalline sulphur. The change is accelerated by a gentle heat, and is attended with evolution of the heat which the sulphur was found to absorb at 200° C. Both these varieties of sulphur are, of course, insoluble in water, and they are not dissolved to any great extent by alcohol and ether; but these, when heated, will dissolve enough to be deposited in *white* silvery needles on cooling. Glacial acetic acid also dissolves sulphur, and deposits it in needles. If the crystalline variety be shaken with a little carbon bisulphide, it rapidly dissolves, and on allowing the solution to evaporate spontaneously, it deposits beautiful octahedral crystals, resembling those of native sulphur (Fig. 165). Ductile sulphur, however, is practically insoluble in carbon bisulphide.

When flowers of sulphur are shaken with carbon bisulphide, a considerable quantity passes into solution, the remainder consisting of the *amorphous*, or insoluble sulphur. Roll sulphur dissolves to a greater extent, and sometimes entirely, in the bisulphide, and distilled sulphur is always easily soluble.

According to the older investigations of Berthelot and others, when a solution of sulphuretted hydrogen (H_2S) is electrolysed the sulphur is separated at the anode, and is therefore the electro-negative element of the compound. This sulphur was found to be soluble in carbon bisulphide. So, also, the sulphur precipitated by an acid from a solution of sulphur in an alkali sulphide is soluble in carbon bisulphide, the assumed reason being that it is electro-negative to the metal with which it was combined.

When, however, a solution of sulphurous acid is electrolysed the sulphur is separated at the cathode showing that in this combination it is electro-positive; this sulphur is insoluble in carbon bisulphide. These observations do not appear to have been satisfactorily confirmed.

It is well known that when a solution of sulphur in carbon bisulphide is exposed

to light sulphur is separated from it, showing that under this influence the soluble variety is converted into the insoluble.

Crystalline or soluble sulphur exists in several forms, of which two are well known. The natural form of crystallised sulphur is derived from the octahedron with a rhombic base (Fig. 165), and it is a modification of this form which sulphur assumes when crystallised from its solutions. But if sulphur be melted in a covered crucible, allowed to cool until the surface has congealed, and the remaining liquid portion poured out after piercing the crust (with two holes, one for admission of air), the crucible will be lined with beautiful needles, which are derived from an oblique prism (Fig. 166). These crystals are brownish-yellow and transparent, when freshly made, but they soon become opaque yellow; and although they retain their prismatic appearance, they have now changed into minute rhombic octahedra, the change being attended with evolution of heat.* On the other hand, if a crystal of octahedral sulphur be exposed for a short time to a temperature of about 230° F. (110° C.), in a boiling saturated solution of common salt, for example, it becomes opaque, in consequence of the formation of a number of minute prismatic crystals in the mass.†

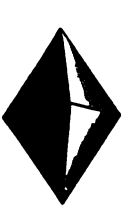


Fig. 165.

Fig. 166.

Both crystalline forms of sulphur may be obtained at the same temperature from *superfused* sulphur, or from a supersaturated solution of sulphur in benzene, by dropping in a crystal of the form required.

The difference between these two forms of crystalline sulphur extends to their fusing-points and specific gravities, the prismatic sulphur fusing at 248° F. (120° C.), and the octahedral sulphur at 239° F. (115° C.), the specific gravity of the prisms being 1.98, and that of the octahedra 2.05.

Roll sulphur, when freshly made, consists of a mass of oblique prismatic crystals, but after being kept for some time, it consists of octahedra, although the mass generally retains the specific gravity proper to the prismatic form. This change in the structure of the mass, taking place when its solid condition prevented the free movement of the particles, gives rise to a state of tension which may account for the extreme brittleness of roll sulphur. If a stick of sulphur be held in the warm hand, it often splits, from unequal expansion. These peculiarities of sulphur deserve careful study, as helping to elucidate the spontaneous alterations in the structure of glass, iron, &c., under certain conditions.

Flowers of sulphur do not present a crystalline structure, but consist of spherical globules composed of insoluble sulphur enclosing soluble sulphur. Hot oil of turpentine dissolves sulphur freely, and when the solution is allowed to stand, the crystals which are deposited whilst the solution is hot have the prismatic form, but as it cools, octahedra are separated.

* Spring has shown that a pressure of 6000 atmospheres converts prismatic sulphur and plastic sulphur into the octahedral variety.

† The change from octahedral to prismatic sulphur is accompanied by the absorption of 650 cals. per gram molecule.

The following table exhibits the chief *allotropic* forms of sulphur:

	Sp. gr.	Fusing-point.	In Carbon Bisulphide.
Octahedral . .	2.05	115° C.	Soluble.
Prismatic . .	1.98	120°	Soluble.
Ductile . . . } Amorphous . . }	1.95	Becomes octahedral.	Insoluble.

The octahedral is by far the most stable of the three, and is the ultimate condition which the others assume. Melted with a little iodine, sulphur remains amorphous when it solidifies, and retains this form for some time.

As has been seen the two forms of sulphur are easily converted the one into the other by changing the conditions under which they exist. This is not an uncommon phenomenon and is quite analogous to the relationship between a solid and the liquid which it becomes when melted. Ice and water, for example, are convertible into each other by varying the temperature, and there is a definite temperature, 0° C., at which they are in equilibrium, that is, neither the ice nor the water increases in quantity. So with the two forms of sulphur: at 96.5° C. both octahedra and prisms may exist in equilibrium, but a slight rise of temperature will increase the mass of the prisms while a slight fall will increase that of the octahedra. The temperature is therefore known as the *transition-point*, and the two forms are said to be *enantiotropes*.

Other varieties of sulphur, such as a black and a red modification, have been described, but it is doubtful if they are pure sulphur. A *colloidal* variety, soluble in water, has been found in the solution formed by passing hydrogen sulphide through an aqueous solution of sulphur dioxide.

Sulphur enters into direct combination with several other elements. It unites with chlorine and with some of the metals, if finely divided, even at the ordinary temperature, and at a high temperature with all the non-metals except nitrogen, and with most metals.

A mixture of 5 parts of iron-powder (*ferrum redactum*) and 3 parts of flowers of sulphur will burn when kindled by a match, leaving a black mass of ferrous sulphide. Zinc-dust mixed with half its weight of sulphur also burns freely, leaving white zinc sulphide.

Fig. 167.

The so-called *Lemery's volcano* was made by mixing iron filings with two-thirds of their weight of powdered sulphur, and burying several pounds of the moist mixture in the earth, when the heat evolved by the rusting of part of the iron provoked the energetic combination of the remainder with the sulphur, and the consequent development of much steam.* Firework compositions containing iron filings and sulphur may cause ignition if damp.

Several metals may be made to burn in sulphur vapour, as in oxygen, by heating the sulphur in a Florence flask, with a gauze burner, so as to keep the flask constantly filled with the brown vapour. Potassium and sodium, introduced in deflagrating spoons, take fire spontaneously in the vapour (Fig. 167). A coil of copper wire glows vividly in sulphur vapour, and becomes converted into a brittle mass of sulphide of copper. When sulphur is exposed to sunshine in an atmosphere of hydride of antimony or arsenic, it becomes converted into hydrosulphuric acid gas and sulphide of antimony or arsenic.

Sulphur dissolves, though slowly, in boiling concentrated nitric and

* *Rust-joint cement* is a mixture of 80 parts iron filings, 1 of sal ammoniac, and 2 of sulphur, made into a paste with water; it is very useful for making the joints of iron tubes air-tight, for it sets into a hard cement, the iron combining with the sulphur.

sulphuric acids, being oxidised by the former into sulphuric acid, and by the latter into sulphur dioxide. It is far more readily converted into sulphuric acid by a mixture of nitric acid and potassium chlorate. The alkalies dissolve sulphur when heated, yielding yellow or red solutions which contain hyposulphites and sulphides of the alkali metals.

There is a very general resemblance in composition between the compounds of sulphur and those of oxygen with the same elements.

Sulphur forms a good example of the diminution which may occur in the vapour-density of an element as the temperature rises, a full discussion of which must be postponed to the chapter on General Principles. Sulphur boils at 444° C., and if its vapour be weighed at a temperature of 480° C., it is found to weigh 6.617 times as much as an equal volume of air at 480° C., so that it is 96 times as heavy as hydrogen, or 1 atom of sulphur would occupy $\frac{1}{3}$ volume. But if the vapour of sulphur be weighed at 1000° C., it is found to weigh only 2.23 times as much as an equal volume of air at the same temperature and pressure, so that it is only 32 times as heavy as hydrogen, and 1 atom of sulphur occupies 1 volume.

Hydrogen Sulphide, or Hydrosulphuric Acid.

$H_2S = 34$ parts by weight = 2 vols.

130. **Sulphuretted hydrogen**, or *hydrogen sulphide*, or *hydrosulphuric acid*, has been already mentioned as occurring in some mineral waters, as at Harrogate. It is also found in the gases emanating from volcanoes, sometimes amounting to one-fourth of their volume. It is a product of the putrefaction of organic substances containing sulphur, and is one of the causes of the sickening smell of drains, &c. Eggs, which contain a considerable portion of sulphur, evolve sulphuretted hydrogen as soon as they begin to change, and hence the association between this gas and the "smell of rotten eggs." The same smell is observed when a kettle boils over upon a coke or coal fire, the hydrogen liberated from the water combining with the sulphur present in the fuel.

Hydrosulphuric acid is also found among the products of destructive distillation of organic substances containing sulphur; it was mentioned among the products from coal, in which it is for the most part combined with the ammonia formed at the same time, producing ammonium sulphide.

It may be produced, though not in large quantity, by the direct union of hydrogen with sulphur vapour at a temperature about the boiling-point of the sulphur, or by passing a mixture of sulphur vapour and steam through a tube filled with red-hot pumice stone (the latter encouraging the action by its porosity). Hydrosulphuric acid is more readily formed by heating a damp mixture of sulphur and wood charcoal, and may be obtained in large quantity by heating a mixture of equal weights of sulphur and tallow or paraffin wax, the latter furnishing the hydrogen.

Preparation of hydrosulphuric acid.—For use in the laboratory, where it is very largely employed in testing for and separating metals, hydrosulphuric acid is generally prepared by decomposing ferrous sulphide with diluted sulphuric acid; $FeS + H_2SO_4 = H_2S + FeSO_4$

To obtain ferrous sulphide, a mixture of 3 parts of iron filings with 2 parts of

flowers of sulphur is thrown, by small portions at a time, into an earthen crucible (A, Fig. 168) heated to redness in a charcoal fire, the crucible being covered after each portion has been added. The iron and sulphur combine, with combustion, and when the whole of the mixture has been introduced, the crucible is allowed to cool, the mass of ferrous sulphide broken out, and a few fragments of it are introduced into a bottle (Fig. 169) provided with a funnel tube for the addition of the acid, and a bent tube for conducting the gas through a small quantity of water, to remove any splashes of ferrous sulphate. From the second bottle the gas is conducted by a glass tube with a caoutchouc joint, either down into a gas-bottle, or into water, or any liquid upon which the gas is intended to act. The fragments of ferrous sulphide should be covered with enough water to fill the gas-bottle to about one-third, and strong sulphuric acid poured by degrees through the funnel, the bottle being shaken until effervescence is observed. An excess of strong sulphuric acid stops the evolution of gas by precipitating a quantity of white anhydrous ferrous sulphate, which coats the sulphide and defends it from the action of the acid. When no more gas is required, the acid liquid should be at once poured away, leaving the fragments of ferrous sulphide at the bottom of the bottle for a fresh operation. The liquid, if set aside, will deposit beautiful green crystals of *copperas* or ferrous sulphate ($FeSO_4.7H_2O$).

Fig. 168.

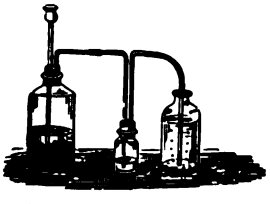


Fig. 169.—Preparation of hydrosulphuric acid.

Since the ferrous sulphide prepared as above generally contains a little metallic iron, the sulphuretted hydrogen is mixed with free hydrogen, which does not generally interfere with its uses. The pure gas may be prepared by heating antimony sulphide (crude antimony) in a flask with hydrochloric acid—

$$Sb_2S_3 + 6HCl = 3H_2S + 2SbCl_3.$$

If hydrochloric acid be diluted with more than 6 molecular proportions of water, it cannot decompose the antimony sulphide; hence, when the sulphide is heated with an acid somewhat stronger than this, the subsequent addition of water reprecipitates the antimony sulphide with the orange colour which it always presents when precipitated.

Generally speaking, it is only the sulphides of those metals which evolve hydrogen from dilute acids that yield H_2S when treated with acids; thus copper and mercury which do not dissolve in HCl with evolution of H, yield sulphides which are not attacked by HCl. Antimony, however, is an exception to this statement.

Properties of hydrosulphuric acid.—This gas is at once distinguished from all others by its disgusting odour. It is one-fifth heavier than air (sp. gr. 1.1912). The gaseous state is not permanent, but a pressure of 17 atmospheres is required to reduce it to a liquid (sp. gr. 0.9), which is colourless, boils at $-62°$ C., and congeals to a transparent solid at $-85°$ C. Water absorbs about three times its volume of sulphuretted hydrogen at the ordinary temperature; both the gas and its solution are feebly acid to blue litmus-paper. The gas is very combustible, burning with a blue flame like that of sulphur, and yielding, as the chief products,

water and sulphurous acid gas, $H_2S + O_3 = H_2O + SO_2$; a little sulphuric acid (H_2SO_4) is also formed, and unless the supply of air be very good, some of the sulphur will be separated; thus, if a taper be applied to a bottle filled with sulphuretted hydrogen, a good deal of sulphur will be deposited upon the sides. This combustibility of sulphuretted hydrogen is of the greatest importance in those processes of chemical manufacture in which this gas is evolved (as in the preparation of ammoniacal salts from gas liquor), enabling it to be disposed of in the furnace instead of becoming a nuisance to the neighbourhood. The gas causes fainting when inhaled in large quantity, and appears much to depress the vital energy when breathed for any length of time even in a diluted state.

When dissolved in water, hydrosulphuric acid is slowly acted upon by the oxygen of the air (particularly in light), which converts its hydrogen into water, and causes a white deposit of sulphur.

This is a great drawback to the use of this indispensable chemical in the laboratory, since the solution of H_2S is soon rendered useless. To obviate it as far as possible, the solution should be made either with boiled water (free from dissolved air), or with water which has already been once charged with the gas and spoilt by keeping, for all the oxygen dissolved in this water will have been consumed by the former portion of gas. The gas should be passed through the water until, on closing the bottle with the hand and shaking violently, the pressure is found to act outwards, showing the water to be saturated with the gas. In an inverted bottle with a greased stopper, the solution may be preserved for some weeks, even though occasionally opened for use. The solution in glycerine keeps better, and is sold as a reagent.

In preparing the solution of hydrosulphuric acid, a certain quantity of the gas always escapes absorption. To prevent this from becoming a nuisance, the bottle containing the water to be charged with gas may be covered with an air-tight caoutchouc cap having two tubes, through one of which passes the glass tube conveying the gas down into the water, and through the other, a tube conducting the excess of gas either into a gas burner, where it may be consumed, or into a solution of ammonia which will absorb it, forming the very useful ammonium sulphide.

Hydrogen sulphide is dissociated by a high temperature, just as water is. Concentrated nitric acid acts upon hydrogen sulphide, oxidising the hydrogen and a part of the sulphur, ammonium sulphate being found in the solution, and a pasty mass of sulphur separated. Chlorine, bromine, and iodine at once appropriate its hydrogen and separate the sulphur. Nitrous acid acts very readily upon hydrogen sulphide, yielding much ammonia; $HO{\cdot}NO + 3H_2S = NH_3 + 2H_2O + S_3$.

In its action upon the metals and their oxides, hydrosulphuric acid resembles hydrochloric and the other hydrogen acids. Many of the metals displace the hydrogen and form metallic sulphides. This usually requires the assistance of heat, but mercury and silver act upon the gas at the ordinary temperature. Thus, if hydrogen sulphide be collected over mercury, the surface of the latter becomes coated with a black film of mercurous sulphide; $H_2S + Hg_2 = H_2 + Hg_2S$. In a similar way the surface of silver is slowly tarnished when exposed to air containing sulphuretted hydrogen, its surface being covered with a black film of silver sulphide. It is on this account that silver plate is so easily blackened by the air of towns. An egg-spoon is always blackened by the sulphur from the egg. Silver coins kept in the pocket with lucifer matches are blackened, from the formation of a little silver sulphide. The original brightness of the coin may be restored by rubbing it with a solution of potassium cyanide, which dissolves the silver sulphide.

Friction with strong ammonia will also remove the tarnish, and its application is safer than that of the poisonous cyanide.

When heated in the gas, several metals displace the hydrogen from it. Thus, potassium acts upon it in a similar manner to that in which it acts upon water, forming *potassium hydrosulphide* (KHS).

Tin removes the whole of the sulphur from hydrosulphuric acid at a moderate heat; $Sn + H_2S = H_2 + SnS$. The hydrogen which is left may be measured, and thus the fact that two volumes of H_2S contain two volumes of hydrogen may be demonstrated.

When hydrosulphuric acid acts upon a metallic oxide, it generally converts it into a sulphide corresponding with the oxide, whilst the hydrogen and oxygen unite to form water. Lead oxide in contact with the gas yields black lead sulphide and water; $PbO + H_2S = PbS + H_2O$. Paper impregnated with a salt of lead is used as a test for the presence of this gas. Thus, if paper be spotted with a solution of lead nitrate (or acetate) it will indicate the presence of even minute quantities of hydrogen sulphide (in impure coal gas, for example) by the brown colour imparted to the spots; $Pb(NO_3)_2 + H_2S = 2HNO_3 + PbS$.

It is in this manner that paints containing white lead (lead carbonate) are darkened by exposure to the air of towns. Cards glazed with white lead, and engravings on paper whitened with that substance, suffer a similar change. Paintings, whether in oil or water-colours, in which lead is an ingredient, are also injured by air containing sulphuretted hydrogen. It has been found that such colours, damaged by the formation of lead sulphide, are restored by the continued action of light and air, the black sulphide becoming oxidised and converted into the white sulphate, $PbS + O_4 = PbSO_4$. In the dark this restoration does not occur, so that it is often a mistake to screen pictures from the light by a curtain.

The action of hydrosulphuric acid upon the chlorides and other haloid salts of the metals generally resembles its action upon the oxides of the same metals.

Most of the sulphides of the metals, like the corresponding oxides, are insoluble in water, but many of the sulphides are also insoluble in diluted acids and in alkalies, so that when hydrosulphuric acid is brought into contact with the solutions of metals, it will in many cases precipitate the metal in the form of a sulphide having some characteristic colour or other property by which the metal may be identified.

Any solution of lead will give a *black* precipitate with solution of H_2S, the lead sulphide being insoluble in dilute acids and in alkalies.

A solution of antimony (tartar-emetic, the tartrate of antimony and potassium, for example), mixed with an excess of hydrochloric acid, gives an *orange*-coloured precipitate (Sb_2S_3) on adding H_2S; but if another portion be mixed with an excess of potash before adding the H_2S, there will be no precipitate, for the antimony sulphide is soluble in alkalies.

Cadmium chloride gives a brilliant *yellow* precipitate of cadmium sulphide.

Zinc sulphate yields a *white* precipitate of zinc sulphide (ZnS), but if a little hydrochloric acid be previously added, no precipitate is formed, the zinc sulphide being soluble in acids. On neutralising the hydrochloric acid with ammonia, the zinc sulphide is at once precipitated.

It is evident that, in a solution containing cadmium and zinc, the metals may be separated by acidifying the liquid with hydrochloric acid and adding excess of hydrosulphuric acid, which precipitates the cadmium sulphide only. On filtering the solution, and adding ammonia, the zinc sulphide is precipitated.

Those sulphides which are soluble in the alkalies are often designated *sulphur-acids*, whilst the sulphides of the alkalies are *sulphur-bases*. These two classes of sulphides combine to form *sulphur-salts* analogous in composition to the oxygen-salts of the same metals. Thus, there have been crystallised, the salts—

Sodium sulphostannate	Na_4SnS_4
„ sulphantimonate	$Na\ SbS_3$
„ sulpharsenate	Na_3AsS_4

Speaking generally, those metals which give feebly acid oxides also give feebly acid sulphides, whilst the sulphides, which correspond with powerful bases are themselves basic, for H_2S is not capable of completely neutralising the alkalies.

The *action of air upon the sulphides* of the metals is often turned to account in chemical manufactures. At the ordinary temperature, the sulphides of those metals which form alkaline oxides (such as sodium and calcium), when exposed to the air in the presence of water, yield sulphite and thiosulphate (hyposulphite). This change is sometimes turned to account for the manufacture of sodium hyposulphite.

When the metal forms a less powerful base with oxygen, the sulphide is often converted into sulphate by exposure to moist air; thus, $CuS + O_4 = CuSO_4$, which is taken advantage of for the separation of copper from its ores.

The black ferrous sulphide (FeS), when exposed to moist air, becomes converted into red ferric oxide, with separation of sulphur, $2FeS + O_3 = Fe_2O_3 + S_2$, a change which enables the gas manufacturer to revive, by the action of air, the ferric oxide employed for removing the sulphuretted hydrogen from coal gas.

When *roasted* in air at a high temperature, the sulphides corresponding with the more powerful bases are converted into sulphates; thus, $ZnS + O_4 = ZnSO_4$, which explains the production of zinc sulphate by roasting blende. But in most cases part of the sulphur is converted into sulphurous acid gas at the same time. Cuprous sulphide, for instance, is partly converted into cupric oxide by roasting, $Cu_2S + O_4 = 2CuO + SO_2$, a change of great importance in the extraction of copper from its ores.

131. *Hydrogen persulphide.*—The composition of this substance is not yet satisfactorily ascertained. The similarity of its chemical properties to those of hydrogen peroxide prompts the wish that its formula may be H_2S_2. Some analyses, however, seem to lead to the formula H_2S_5, but since the persulphide is a liquid capable of dissolving free sulphur, which is not easily separated from it, there is much difficulty in determining the exact proportion of this element with which the hydrogen is combined.

When equal weights of slaked lime and sulphur are boiled with water, an orange-coloured liquid is formed, which contains calcium hyposulphite, calcium disulphide, and calcium pentasulphide (CaS_5); $3CaO + S_6 = CaS_2O_3 + 2CaS_2$.

When HCl is added to the filtered solution an abundant precipitation of sulphur occurs, and much H_2S is evolved; $CaS_2 + 2HCl = CaCl_2 + H_2S + S$. But if the solution be poured by degrees into a slightly warm mixture of HCl with twice its bulk of water, and constantly stirred, a yellow heavy oily liquid collects at the bottom, which is the hydrogen persulphide; $CaS_2 + 2HCl = H_2S_2(?) + CaCl_2$. The acid having been kept in excess, the persulphide has been preserved from the decomposition which it suffered in the presence of the alkaline solution in the former experiment. For the hydrogen persulphide very closely resembles the peroxide in the facility with which it may be decomposed into hydrosulphuric acid and sulphur; it undergoes spontaneous decomposition even in sealed tubes, and the hydrosulphuric acid then becomes liquefied by its own pressure. Most of

the substances, the contact of which promotes the decomposition of H_2O_2, have the same effect upon the persulphide. This compound has a peculiar odour, which affects the eyes; of course, its vapour is mixed with H_2S resulting from its decomposition. Its specific gravity is 1.73.

Oxides of Sulphur.

132. Only two important compounds of sulphur with oxygen have been obtained in the separate state—viz., *sulphurous anhydride* (SO_2) and *sulphuric anhydride* (SO_3). *Sulphur sesquioxide* (S_2O_3) and *persulphuric oxide* (S_2O_7) also exist.

Sulphur Dioxide or Sulphurous Anhydride.

$SO_2 = 64$ parts by weight $= 2$ vols.

133. In nature, sulphur dioxide (sulphurous acid gas) is but rarely met with; it exists in the gases issuing from volcanoes. Although constantly discharged into the air of towns by the combustion of coal (containing sulphur), it is so easily oxidised and converted into sulphuric acid that no considerable quantity is ever found in the atmosphere. Sulphurous acid gas has been already mentioned as the sole product of the combustion of sulphur in dry air or oxygen,* but it is generally prepared in the laboratory from sulphuric acid, by heating it with metallic copper, $2H_2SO_4 + Cu = CuSO_4 + 2H_2O + SO_2$.

20 grams of copper clippings are heated in a flask with 110 c.c. of strong H_2SO_4, the gas being conducted by a bent tube down to the bottom of a dry bottle closed with a perforated card (see Fig. 150, p. 177). Some time elapses before the gas is evolved; for sulphuric acid attacks copper only at a high temperature; but when the evolution of gas fairly begins it proceeds very rapidly, so that it is necessary to remove the flame from under the flask. The gas will contain a little suspended vapour of sulphuric acid, which renders it turbid.

When the operation is finished, and the flask has been allowed to cool, it will be found to contain a grey crystalline powder at the bottom of a brown liquid. The latter is the excess of H_2SO_4 used, and retains very little copper, since cupric sulphate is insoluble in the strong acid. If the liquid be poured off, and the flask filled up with water, and set aside for some time, the crystalline powder will dissolve, forming a blue solution of sulphate of copper, yielding that salt in fine prismatic crystals by evaporation and cooling. The dark powder remaining undissolved after extracting the whole of the sulphate, consists chiefly of cuprous sulphide (Cu_2S), the production of which is interesting, as showing how far the de-oxidising effect of the copper may be carried in this experiment.

Sulphur dioxide is a very heavy (sp. gr. 2.25) colourless gas, characterised by its odour of burning brimstone. It condenses to a clear liquid at 0° F. (the temperature of a mixture of ice and salt, – 18° C.) even at the ordinary pressure of the air, and has been frozen to a colourless crystalline solid at – 76° C. The liquid has the sp. gr. 1.4 at 15° C., and boils at – 8° C. As would be anticipated from its comparatively high boiling-point SO_2 is a very imperfect gas (p. 28). The cold produced by the evaporation of the liquefied gas is about 6500 cals. per gram mol., and the liquid finds application in some forms of freezing-machines. The critical temperature is 157° C., and the pressure 79 atmospheres.

The liquefaction of the gas is easily exhibited by passing it down to the bottom of a tube (A, Fig. 170) closed at one end, and surrounded with a mixture of

* According to Berthelot, a notable quantity of SO_3 is produced at the same time.

pounded ice with half its weight of salt. The tube should have been previously drawn out to a narrow neck at B, which may afterwards be sealed by the blow-pipe, the lower part of the tube being still surrounded by the freezing-mixture. The tube need not be very strong, for at the ordinary temperature the vapour exerts a pressure of only 2.5 atmospheres. Liquid sulphur dioxide is a convenient agent for producing (by its rapid evaporation) the low temperature (– 39° F.) required to effect the solidification of mercury. A small globule of this metal may readily be frozen by dropping some liquid sulphur dioxide upon it in a watch-glass placed in a strong draught of air. The tube containing the sulphur dioxide should be held in a woollen cloth or glove. The attractive experiment of freezing water in a red-hot crucible may also be made with the liquid. A platinum crucible being heated to redness, and some liquid sulphur dioxide poured into it, from a tube which has been cooled for half an hour in ice and salt, the liquid becomes surrounded with an atmosphere of sulphurous acid gas, which prevents its contact with the metal (assumes the *spheroidal* state), and its temperature is reduced by its own evaporation to so low a degree that a little water allowed to flow into it will at once become converted into opaque ice. Liquid SO_2 is now sold in glass "siphons" similar to those in which soda-water is supplied, and these form a convenient store of the gas.

Fig. 170.

Sulphurous acid gas is very easily absorbed by water, as may be shown by pouring a little water into a bottle of the gas, closing the bottle with the palm of the hand, and shaking it violently, when the diminished pressure due to the absorption of the gas will cause the bottle to be sustained against the hand by the pressure of the atmosphere. Water absorbs 43.5 times its bulk of the gas at the ordinary temperature. The solution is believed to contain sulphurous acid, H_2SO_3, formed by the reaction $H_2O + SO_2 = H_2SO_3$, but this body has not been obtained in the separate state. If the solution be exposed to a low temperature, a crystallised hydrate, $H_2SO_3.14H_2O$, is obtained; this melts at 2° C. When the solution of sulphurous acid is kept for some time in a bottle containing air, its smell gradually disappears, the acid absorbing oxygen and becoming converted into sulphuric acid.

Sulphur dioxide, like carbon dioxide, possesses in a high degree the power of extinguishing flame. A taper is at once extinguished in a bottle of the gas, even when containing a considerable proportion of air. One of the best methods of extinguishing burning soot in a chimney consists in passing up sulphurous acid gas by burning a few ounces of sulphur in a pan placed over the fire.

The principal uses of sulphur dioxide depend upon its property of bleaching many animal and vegetable colouring-matters. Although a far less powerful bleaching agent than chlorine, it is preferred for bleaching silks, straw, wool, sponge, isinglass, baskets, &c., which would be injured by the great chemical energy of chlorine. The articles to be bleached are moistened with water and suspended in a chamber in which sulphurous acid gas is produced by combustion of sulphur. The colouring-matters do not appear in general to be decomposed by the acid, but rather to form colourless combinations with it, for in course of time the original colour often reappears, as is seen in straw, flannel, &c., which becomes yellow from age, the sulphurous acid probably being oxidised into sulphuric acid. Stains of fruit and port wine on linen are

conveniently removed by solution of sulphurous acid. Hops are *sulphured* by exposure to fumes of burning sulphur with the object of improving their appearance.

The red solution obtained by boiling a few chips of logwood with river water (distilled water does not give so fine a colour) serves to illustrate the bleaching properties of sulphurous acid. A few drops of the solution of the acid will at once change the red colour of the solution to a light yellow; but that the colouring power is suspended, and not destroyed, may be shown by dividing the yellow liquid into two parts, and adding to them, respectively, potash and diluted sulphuric acid, which will restore the colour in a modified form. To contrast this with the complete decomposition of the colouring-matter, a little sulphurous acid may be added to a weak solution of the potassium permanganate, when the splendid red solution at once becomes perfectly colourless, and neither acid nor alkali can effect its restoration.

Fig. 171.

If a bunch of damp coloured flowers be suspended in a bell-jar over a crucible containing a little burning sulphur (Fig. 171), many of the flowers will be completely bleached by the sulphurous acid; and by plunging them afterwards into diluted sulphuric acid and ammonia, their colours may be partly restored with some very curious modifications.

Another very useful property of sulphurous acid is that of arresting fermentation (or putrefaction), apparently by killing the vegetable or animal growth which is the cause of the fermentation. This is commonly designated the *antiseptic* or *antizymotic* property of sulphurous acid, and is turned to account when casks for wine and beer are *sulphured* in order to prevent the action of any substance contained in the pores of the wood, and capable of exciting fermentation, upon the fresh liquor to be introduced. If a little solution of sugar be fermented with yeast in a flask provided with a funnel tube (Fig. 172), a solution of sulphurous acid poured in through the latter will at once arrest the fermentation. The salts of sulphurous acid (sulphites) are also occasionally used to arrest fermentation, in the manufacture of sugar, for instance. Clothes are sometimes fumigated with sulphurous acid gas to destroy vermin, and the air of rooms is disinfected by burning sulphur in it, 4 lbs. of sulphur being recommended for every 1000 cubic feet of space.

Fig. 172.

The disposition of sulphurous acid to absorb oxygen and pass into sulphuric acid, renders it a powerful de-oxidising or reducing agent. Solutions of silver and gold are reduced to the metallic state by sulphurous acid and sulphites. As usual, however, the reducing power of sulphur dioxide is only a comparative phenomenon. Towards several substances the acid behaves as an oxidising agent, a noteworthy case being its reaction with hydrogen sulphide, which (in presence of water) occurs in the sense of the equation, $2H_2S + SO_2 = 2H_2O + S_3$.

An aqueous solution of stannous chloride gives a precipitate of stannic sulphide with sulphurous acid.

If a solution of sulphurous acid be heated for some time in a sealed tube at 150° C., one portion of the acid de-oxidises another, sulphur is separated, and sulphuric acid formed; $3H_2SO_3 = 2H_2SO_4 + H_2O + S$.

SO_2 and NH_3 combine to form two solid compounds $(NH_3)_2SO_2$ and $NH_3.SO_2$.

The unsaturated character of SO_2 finds illustration in the fact that chlorine combines with an equal volume of the gas, under the influence of bright sunshine, or in presence of charcoal, to produce a colourless liquid, the vapour of which is very acrid and irritating to the eyes. This is the chloranhydride (p. 191) of sulphuric acid, *sulphuryl chloride*, SO_2Cl_2. Its decomposition by water occurs in two stages: (1) $SO_2Cl_2 + H_2O = SO_2.Cl.OH + HCl$; (2) $SO_2.Cl.OH + H_2O = SO_2.OH.OH + HCl$; the final products being sulphuric and hydrochloric acids, so that the formula $SO_2.OH.OH$ for sulphuric acid is justified. The *chloride of thionyl*,* or *sulphurosyl chloride*, $SOCl_2$, is a colourless volatile liquid obtained by the action of sulphurous acid gas on phosphorus pentachloride. It is decomposed by water, yielding hydrochloric and sulphurous acids, being the chloranhydride of the latter.

Potassium and sodium, when heated in sulphur dioxide, burn vividly, producing the oxides and sulphides of the metals. Iron, lead, tin, and zinc are also converted into oxides and sulphides when heated in the gas; $SO_2 + Zn_3 = ZnS + 2ZnO$.

Lead peroxide, PbO_2, is the best absorbent for SO_2 with which it combines (with incandescence in the pure gas) to form lead sulphate: $PbO_2 + SO_2 = PbSO_4$.

That sulphur dioxide contains its own volume of oxygen is best shown by burning sulphur in a given volume of oxygen in the apparatus represented in Fig. 173.

The stopper A having been removed, mercury is poured into the open limb of the U-tube until it stands at a point just below the bulb B, the air in which is then displaced by oxygen. A pellet of sulphur is placed in the metal spoon attached to the stopper and the latter is inserted directly the tube delivering the oxygen has been removed. A platinum helix rests upon the sulphur and is now heated to redness by a current of electricity passed through the wires attached to the spoon and the helix. When the sulphur has burnt itself out and the apparatus has cooled, it will be found that the volume of gas has not varied, showing that the SO_2 produced contains its own volume of oxygen. To relieve the pressure produced by the heat of the combustion, it is well to diminish the initial pressure, after the gas has been measured, by drawing off some of the mercury through the stop-cock C.

Fig. 173.
Composition of SO_2 gas.

Sulphites.—The acid character of sulphurous acid is rather feeble, although stronger than that of carbonic acid. There is much general resemblance between the sulphites and carbonates in point of solubility, the sulphites of the alkali metals being the only salts of sulphurous acid which are freely soluble in water. Sulphurous acid, $SO(OH)_2$, being dibasic like carbonic acid, forms two classes of salts, the normal sulphites (for example, sodium sulphite, Na_2SO_3) and acid sulphites (as hydrogen potassium sulphite, $KHSO_3$).

Sodium sulphite is extensively manufactured for the use of the paper-maker, who employs it as an *antichlore* for *killing the bleach*, that is, neutralising the excess of chlorine after bleaching the rags with chloride of lime (see p. 183); $Na_2SO_3 + H_2O + Cl_2 = Na_2SO_4 + 2HCl$. It is prepared by passing sulphurous acid gas over damp crystals of sodium carbonate, when CO_2 is expelled, and sodium sulphite formed, which is dissolved in water and crystallised. It forms oblique prisms, having the composition $Na_2SO_3.7Aq$, which effloresce in the air, becoming

* Θεῖον, *sulphur*.

opaque, and slowly absorbing oxygen, passing into sodium sulphate (Na_2SO_4). Its solution is slightly alkaline to test-papers.

For the manufacture of sodium sulphite the SO_2 is obtained either by the combustion of sulphur or by heating sulphuric acid with charcoal: $2H_2SO_4 + C = 2H_2O + CO_2 + 2SO_2$. The carbon dioxide of course will not interfere with this application of the sulphur dioxide.

The existence of sulphurosyl chloride, $SO.Cl_2$, and its behaviour with water justify the formula $SO(OH)_2$ for sulphurous acid. There is some evidence, derived from organic chemistry (see *Sulphonic Acids*), that the metallic sulphites are not derived from $SO(OH)_2$, but from an acid of the form $\begin{matrix} O \\ O \end{matrix}\!\!\gg S\!<\!\begin{matrix} OH \\ H \end{matrix}$, which may be regarded as the parent substance of the sulphonic acids, and may therefore be termed *sulphonic* acid. The potassium sulphite is supposed to be $O_2S.OK.K$, and not SO.OK.OK. Two potassium-sodium sulphites have been prepared which differ in properties and appear to be $O_2S.OK.Na$ and $O_2S.ONa.K$ respectively.

Solutions of the sulphites absorb nitric oxide in the cold, yielding *nitrosulphites*, such as the potassium salt $K_2SO_3.2NO$. At higher temperatures the sulphites reduce NO to N_2O.

Pyrosulphites, derived from hypothetical *pyrosulphurous acid*, $H_2S_2O_5$, crystallise from hot strong solutions of bisulphites, $2KHSO_3 = K_2S_2O_5 + H_2O$. Possibly they are compounds of normal sulphites with $SO_2 - K_2SO_3.SO_2$.

Sulphur Trioxide or Sulphuric Anhydride.

$SO_3 = 80$ parts by weight.

Sulphur dioxide and oxygen combine to form sulphur trioxide when passed through a tube containing heated platinum or certain metallic oxides, such as those of iron and chromium, the action of which in promoting the combination is not thoroughly understood. The reaction is exothermic, evolving some 103,000 cals. per 80 grams of SO_3 formed.

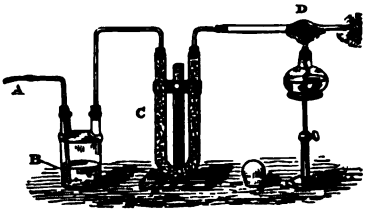


Fig. 174.

The combination may be shown by passing oxygen from the tube A (Fig. 174), connected with a gas-holder, through a strong solution of sulphurous acid (B), so that it may take up a quantity of SO_2; afterwards through a tube (C) containing pumice-stone soaked with oil of vitriol to remove the water; and then through a bulb (D) containing platinised asbestos (see p. 98). The mixture of the gases issuing into the air is quite invisible, but when the bulb is gently heated combination occurs, and dense white clouds are formed in the air, from the combination of the sulphuric anhydride (SO_3) produced, with the atmospheric moisture. The clouds are best shown by conducting them, through a bent tube attached to D, into a large flask.

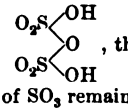
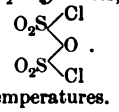
Pure sulphur trioxide, prepared by repeated distillation out of contact with moisture, is a mobile liquid which crystallises when cooled, in long transparent prisms like nitre, which fuse at 14°.8 C. and boil at 46° C. At temperatures below 25° C. these crystals easily change, especially if they have absorbed a little water, into an opaque, fibrous, crystalline mass which does not fuse, but vaporises at about 50° C., the vapour condensing again to the prismatic variety which melts at 14.8°. The formula of the fibrous form appears to be S_2O_6, and it is much less active than the prismatic form (SO_3). When sulphuric acid in small quantity is added to SO_3 it dissolves it, and on cooling to 8° C. crystals

of $H_2SO_4.3SO_3$ are deposited. When more H_2SO_4 is added, it forms *pyrosulphuric acid*, $H_2SO_4.SO_3$ or $H_2S_2O_7$ (m.p. 35° C.). SO_3 can dissolve much SO_2.

When exposed to air, sulphur trioxide emits strong white fumes, its vapour combining with the moisture of the air. It soon deliquesces and becomes sulphuric acid—$SO_3 + H_2O = H_2SO_4$.

When thrown into water it hisses like red-hot iron, from the sudden formation of steam. The vapour is decomposed into SO_2 and O, when passed through a red-hot tube; but if the tube contain platinum, or another "contact substance," the vapour is only in a dissociated state, for the SO_2 and O recombine on cooling in contact with the platinum. Phosphorus burns in its vapour, combining with the oxygen and liberating sulphur. Baryta glows when heated in the vapour, combining with it to form barium sulphate, unless both be quite dry.

Sulphuric anhydride mixes in all proportions with sulphuric acid, the mixture being known as *fuming sulphuric acid*. The melting-point of the mixture varies with the percentage of SO_3 in it; that containing 80 per cent. is the most convenient for use, as it remains liquid at ordinary temperature. Fuming sulphuric acid finds extended application in Organic Chemistry for making sulphonic acids (*q.v.*). By gently warming it, much SO_3 can be distilled from it for small experiments.

The *pyrosulphuric* acid, or *anhydrosulphuric acid*, $H_2S_2O_7$, referred to above, contains 45 per cent. of SO_3 and is solid at ordinary temperature; it may be regarded as SO_3 which has insufficient water to form H_2SO_4 ($H_4S_2O_8$), and since the acid chloride $S_2O_5Cl_2$ (formed by the action of excess of PCl_5 on H_2SO_4) exists, its constitution may be represented as  , the chloride being  . An acid containing a larger proportion of SO_3 remains liquid at low temperatures.

Sulphuric anhydride is capable of combining with olefiant gas (C_2H_4) and similar hydrocarbons, and absorbs these from mixtures of gases. In the analysis of coal gas, a fragment of coke wetted with fuming sulphuric acid is passed up into a measured volume of the gas standing over mercury to absorb these illuminating hydrocarbons. SO_3 also combines with HCl, forming $SO_2.Cl.OH$, which may also be obtained by distilling sulphuric acid with phosphoric chloride—

$$3SO_2(OH)_2 + PCl_5 = 3(SO_2.Cl.OH) + PO_2.OH + 2HCl.$$

An interesting method of obtaining the sulphuric anhydride consists in pouring 2 parts by weight of oil of vitriol over 3 parts of phosphoric anhydride, contained in a retort cooled in ice and salt, and afterwards distilling at a gentle heat, when the phosphoric anhydride retains water, and the SO_3 may be condensed in a cooled receiver.

Sulphuric Acid, or Hydrogen Sulphate.

H_2SO_4 or $SO_2(OH)_2 = 98$ parts by weight.

134. More than four centuries ago the alchemist Basil Valentine subjected *green vitriol*, as it was then called (sulphate of iron), to distillation, and obtained an acid liquid which he named *oil of vitriol*. The process discovered by this laborious monk is even now in use at Nordhausen in Saxony, and the *Nordhausen oil of vitriol* was at one

time an important article of commerce. The crystals of ferrous sulphate ($FeSO_4.7H_2O$) exposed to the air absorb oxygen, and become *basic ferric sulphate;* $6FeSO_4 + O_3 = 2Fe_2(SO_4)_3.Fe_2O_3$.

When this salt is partially dried, and distilled in earthenware retorts, a mixture of sulphuric acid and sulphuric anhydride distils over, and constitutes Nordhausen or *fuming sulphuric acid;* $Fe_2(SO_4)_3 + 2H_2O = Fe_2O_3 + 2H_2SO_4 + SO_3$. The ferric oxide ($Fe_2O_3$) which is left in the retorts, is the red powder known as *colcothar*, which is used for polishing plate glass and metals.

The green vitriol employed for preparing the Nordhausen acid was obtained from iron pyrites (FeS_2). A particular variety of this mineral, *white pyrites* (or efflorescent pyrites), when exposed to moist air, undergoes oxidation, yielding ferrous sulphate and sulphuric acid; $FeS_2 + H_2O + O_7 = FeSO_4 + H_2SO_4$.

Large masses of this variety of pyrites in mineralogical cabinets may often be seen broken up into small fragments, and covered with an acid efflorescence of ferrous sulphate from this cause. Ordinary iron pyrites is not oxidised by exposure to the air unless it be first subjected to distillation in order to separate a portion of the sulphur which it contains.

The first step towards the discovery of the process which, until within the last few years, has been the only profitable one by which this acid could be manufactured on a large scale was also made by Valentine, when he prepared his *oleum sulphuris per campanum*, by burning sulphur under a bell-glass over water, and evaporating the acid liquid thus obtained. The same experimenter also made a very important advance when he burnt a mixture of sulphur, antimony sulphide and nitre under a bell-glass placed over water; but it was not until the middle of the eighteenth century that it was suggested by some French chemists to burn the sulphur and nitre alone over water; a process by which the acid appears actually to have been manufactured upon a pretty large scale. The substitution of large chambers of lead for glass vessels by Dr. Roebuck was a great improvement on the process, and about the year 1770 the preparation of the acid formed an important branch of manufacture; since then the process has been steadily improving until, at the present time, a very large quantity is manufactured by this method. The diminution in the price of oil of vitriol well exhibits the progress of improvement in its production, for the original *oil of sulphur* appears to have been sold for about half a crown an ounce, and that prepared by burning sulphur with nitre in glass vessels at the same price per pound; but when leaden chambers were introduced, the price fell to a shilling per pound, and at present oil of vitriol can be purchased at the rate of five farthings per pound.

The description of the present "chamber process" of manufacture will be best understood after a consideration of the principles of the chemical changes upon which it depends.

It has been seen that when sulphur is burnt in air sulphur dioxide is produced. When this acts on nitric acid, in the presence of water, sulphuric acid and nitric oxide are produced, $3SO_2 + 2HNO_3 + 2H_2O = 3H_2SO_4 + 2NO$.* The nitric oxide, in contact with air becomes nitric peroxide, $NO + O = NO_2$, which, in the presence of H_2O, serves to convert a further quantity of SO_2 into H_2SO_4, $SO_2 + NO_2 + H_2O =$

* According to some authorities, N_2O_3 is the oxide of nitrogen produced; since, however, it has been shown that this compound can only exist at low temperatures, the view that nitric oxide is the oxide formed in the chambers is here adopted.

$H_2SO_4 + NO$; nitric oxide is thus regenerated and serves to convert more SO_2 into sulphuric acid if the requisite quantities of air and steam be supplied, the two last equations being repeated.

When the supply of steam is deficient, nitrosyl sulphate is found deposited in crystals (*chamber crystals*) in the sulphuric acid chambers. This has been formed according to the equation $2SO_2 + 2NO_2 + O + H_2O = 2SO_2.OH.ONO$. In the presence of a further quantity of SO_2 and H_2O the nitrosyl sulphate is decomposed thus—

$$2SO_2OH.ONO + SO_2 + 2H_2O = 3H_2SO_4 + 2NO.$$

It is generally believed that these two equations represent the reactions in the chamber rather than those quoted above.

It appears, therefore, that NO may be employed to absorb oxygen from the air and to convey it to the SO_2, so that, theoretically, an unlimited quantity of sulphur might be converted into sulphuric acid by a given quantity of NO, with a sufficient supply of air and steam.

The actual reactions involved in this process have received much attention, and a full discussion of the probabilities will be found in works on sulphuric acid manufacture.

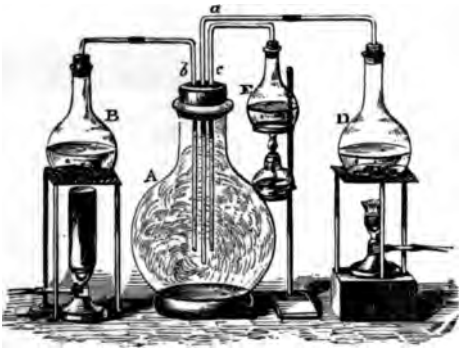


Fig. 175.—Preparation of sulphuric acid.

To illustrate the chemical principles of the manufacture of sulphuric acid, a large glass flask or globe (A, Fig. 175) is fitted with a cork through which are passed (*a*) a tube connected with a flask (D) containing copper and strong sulphuric acid for evolving SO_2; (*b*) a tube connected with a flask (B) containing copper and dilute nitric acid (sp. gr. 1.2) for supplying nitric oxide; (*c*) a tube proceeding from a small flask (E) containing water.

On heating the flask containing nitric acid and copper, the NO passes into the globe and combines with the oxygen of the air,* filling the globe with a red mixture of nitric peroxide and nitrous anhydride. The nitric oxide flask may then be removed. Sulphur dioxide is now generated by heating the flask containing sulphuric acid and copper; the SO_2 soon decolourises the red gas, the contents of the globe becoming colourless, and the crystalline compound forming abundantly on the sides; the sulphur dioxide flask may then be removed. Steam is sent into the globe from the flask containing water, when the crystalline compound dissolves, and sulphuric acid collects at the bottom of the globe.

If the experiment be repeated, the steam being introduced simultaneously with the sulphur dioxide, no crystalline compound will be formed, the sulphur dioxide being at once converted into sulphuric acid.

Since the cork is somewhat corroded in this experiment, it is preferable to have the mouth of the flask ground and closed by a ground glass plate, perforated with holes for the passage of the tubes. The perforations are easily made by placing the glass plate flat against the wall and piercing it with the point of a revolving rat's-tail file dipped in turpentine; the file is then gradually worked through the hole until the latter is of the required size.

The process employed for the manufacture of English oil of vitriol will now be easily understood.

A series of chambers (about 100 ft. × 20 ft. × 20 ft., shown in transverse section at F, Fig. 176), is constructed of leaden plates, the edges

* The operation is, of course, more striking if oxygen is employed instead of air, the globe in Fig. 175 being filled with oxygen by displacement at the commencement.

of which are united by autogenous soldering (that is, by fusing together their edges without solder, which would be rapidly corroded by the acid vapours.) The bottom or *saucer* (G) of the chamber is not attached to

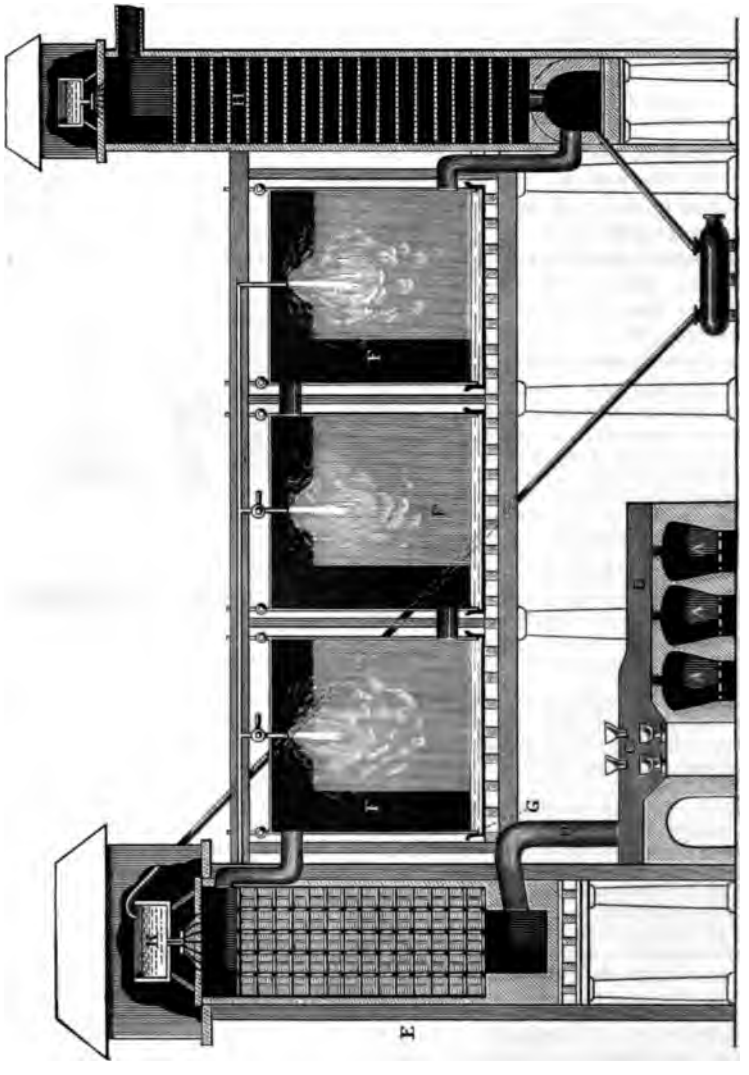


Fig. 176.—Sulphuric acid chambers.

the upper portion or *curtain* (F), the sulphuric acid which collects in the saucer serving to seal the communication between the interior of the chamber and the outer air. A framework of timber supports the curtain.

The *sulphurous acid gas* is generated by burning iron pyrites* or

* $2FeS_2 + O_{11} = Fe_2O_3 + 4SO_2$.

sulphur in suitable furnaces (A) adjoining the chambers, and so arranged that the gas produced may be mixed with about the proper quantity of *air* to furnish the oxygen required for its conversion into sulphuric acid.

Nitric acid vapour is evolved from a mixture of sodium nitrate and oil of vitriol (see page 89) contained in iron *nitre pots* (C) which are heated by being placed in the flue (B), leading from the pyrites burners to the chamber, so that the nitric acid is carried into the chambers with the current of sulphurous acid gas and air (through D).

Jets of steam are introduced at different parts of the chambers from an adjacent boiler.

The sulphurous acid gas acts upon the nitric acid vapour, in the presence of the water, forming nitric oxide and sulphuric acid which rains down into the water on the floor of the chambers. If the NO were permitted to escape from the chambers, and a fresh quantity of nitric acid vapour introduced to oxidise another portion of sulphur dioxide, 2 molecules (170 parts by weight) of sodium nitrate would be required to furnish the nitric acid for the conversion of 2 atoms (64 parts by weight) of sulphur, whereas, in practice, only 4 parts by weight of nitrate are employed for 96 parts of sulphur.

The nitrogen of the air takes no part in the change; and since the oxygen consumed in converting the sulphur into sulphuric acid is accompanied by four times its volume of nitrogen, there is a very large accumulation of this gas in the chambers, and provision must be made for its removal in order to allow space for those gases which take part in the change. The obvious plan would appear to be the erection of a simple chimney for the escape of the nitrogen at the opposite end of the chamber to that at which the sulphurous acid gas and air enter it, and this plan was formerly adopted; but the nitrogen carries off with it a portion of the oxides of nitrogen which are so valuable in the chamber, and to save this the escaping nitrogen is now generally passed through a lead-lined tower (Gay-Lussac's tower) (H) filled with perforated stoneware plates, through which oil of vitriol (sp. gr. 1.72) is allowed to trickle: the oil of vitriol absorbs the nitrogen oxides, and flows into a cistern (*acid egg*), wherefrom it is forced up, by air pressure, to a cistern (K) at the top of another tower (Glover's tower) (E) packed with acid-proof bricks, through which the hot SO_2 and air are made to pass as they enter, when they take up the nitrogen oxides from the "nitrous vitriol," and carry them into the chamber.

A saving of over 50 per cent. of the weight of sodium nitrate used is thus effected.

The sulphuric acid is allowed to collect on the floor of the chamber until it has a specific gravity of about 1.6, and contains 70 per cent. of oil of vitriol (H_2SO_4). If it were allowed to become more concentrated than this, it would both attack the lead and absorb some of the oxides of nitrogen in the chamber, so that it is now drawn off.

This acid (chamber acid) is quite strong enough for some of the applications of sulphuric acid, particularly for that which consumes the largest quantity in this country, viz., the conversion of common salt into sodium sulphate as a preliminary step in the manufacture of carbonate of soda. To save the expense of transporting the acid for this purpose, the *vitriol chambers* form part of the plant of the alkali works.

To convert this weak acid into the ordinary oil of vitriol of commerce,

it is run off into shallow leaden pans set in brickwork and supported on iron bars over the flue of a furnace, where it is heated until so much water has evaporated that the specific gravity of the acid has increased to 1.72. The concentration cannot be carried further in leaden pans, because the strong acid acts upon the lead, and converts it into sulphate—

$$2H_2SO_4 + Pb = PbSO_4 + 2H_2O + SO_2.$$

When a Glover's Tower is used the whole of the chamber acid is passed down the tower together with the nitrous vitriol. The chamber acid is thus concentrated by the heat of the furnace gases to sp. gr. 1.72 and the gases are at the same time cooled.

The acid of 1.72 sp. gr. contains about 80 per cent. of true oil of vitriol, and is largely employed for making superphosphate of lime, and in other rough chemical manufactures. It is technically called *brown acid* (brown oil of vitriol, B.O.V.), having acquired a brown colour from organic matter accidentally present in it.

To convert this brown acid into commercial oil of vitriol, it is boiled down, either in glass retorts or platinum stills, when water distils over, accompanied by a little sulphuric acid, and the acid in the retort becomes colourless, the brown carbonaceous matter being oxidised by the strong sulphuric acid, with formation of carbonic and sulphurous acid gases. When dense white fumes of oil of vitriol begin to pass over, showing that all the superfluous water has been expelled, the acid is drawn off by a siphon. The strongest acid obtainable by this process still contains about 2 per cent. of water, formed by the decomposition of some of the H_2SO_4 into H_2O and SO_3, which escapes as vapour.

The cost of the acid is very much increased by this concentration. It cannot be conducted in open vessels, partly on account of the loss of sulphuric acid, partly because concentrated sulphuric acid absorbs moisture from the open air even at the boiling-point. The loss by breakage of the glass retorts is very considerable, although it is reduced as far as possible by heating them in sand, and keeping them always at about the same temperature by supplying them with hot acid. But the boiling-point of the concentrated acid is very high (640° F., 338° C.), and the retorts consequently become so hot that a current of cold air or an accidental splash of acid will frequently crack them at once. Moreover, the acid boils with *succussion* or violent bumping, caused by sudden bursts of vapour, which endanger the safety of the retort.

With platinum stills the risk of fracture is avoided, and the concentration may be conducted more rapidly, the brown acid (sp. gr. 1.72) being admitted at the top. and the oil of vitriol (sp. gr. 1.84) drawn off by a platinum siphon from the bottom of the still, which is protected from the open fire by an iron jacket. But since a platinum still costs £2000 or £3000, the interest upon its value increases the cost of production of the acid. It is stated to be economical to protect the platinum from the slight action of the vitriol on it by a lining of gold, which is less attacked.

When the perfectly pure acid is required, it is actually distilled so as to leave the solid impurities (sulphate of lead, &c.) in the retort. Some fragments of rock crystal should be introduced into the retort to moderate the bursts of vapour, and heat applied by a ring gas-burner with somewhat divergent jets.

Commercial sulphuric acid is liable to contain nitrogen oxides, lead sulphate, arsenic (from the iron pyrites burnt in the kilns), and iron. Arsenic-free acid may be made by passing H_2S through the diluted acid, filtering off the precipitate of As_2S_3, and concentrating. It is generally made, however, by using sulphur in the kilns in place of pyrites. Nitrogen oxides are eliminated by adding a little ammonium sulphate during concentration; $NO + NO_2 + (NH_4)_2SO_4 = N_4 + H_2SO_4 + 3H_2O$. To eliminate iron and lead sulphate the acid must be distilled.

For many years it has been the dream of the sulphuric acid maker to

combine sulphur dioxide and atmospheric oxygen, by the method described at p. 222 for making sulphuric anhydride, and to absorb the product in water to obtain sulphuric acid. In such a process the "contact substance" has the same function as that of the nitric oxide in the chamber-process, that is to say, it acts as a carrier of oxygen from the air to the sulphur dioxide, although in what manner is unknown. The contact-substance has the great advantage over nitric oxide that, being a solid, it requires less room in which to do its work, and is not liable to loss by leakage. Thus the unit of plant might be expected to be considerably smaller in a "contact-process" for making sulphuric acid than in the chamber-process. An economy of greater importance than the saving of interest on plant, however, consists in the possibility of making by the contact-process strong sulphuric acid, or even a fuming acid, at once, thus eliminating the cost of concentration; for it is obvious that by adjusting the proportion of water by which the sulphuric anhydride is absorbed, an acid of any degree of concentration may be obtained.

Unfortunately, there are several conditions which affect unfavourably the combination of SO_2 and O in the contact-process. The only contact-substance which has proved so far sufficiently active in inducing the combination is platinum, most economically used by spreading it over a large surface as in the form known as platinised asbestos (p. 98). The activity of this material, however, rapidly diminishes if the gases contain impurities, because these are either deposited on the platinum or they combine with it and render it ineffective. Such impurities are said to "poison" the metal, and the worst of them in this respect are compounds of arsenic, phosphorus, and mercury. The first of these is nearly always present in the pyrites burnt for the production of SO_2, and, passing into the gases, is sufficient, together with the dust arising from the pyrites burners, to render the platinum useless in a very short time. It was the necessity for constantly renewing the platinum by dissolving it from the asbestos by aqua-regia, and again precipitating it thereon, that prevented the success of the contact-process in the past.

Another difficulty to be met in the contact-process (or *catalytic process*) arises from the fact that the heat evolved when SO_2 and O combine (p. 222) is apt to accumulate until the temperature of the contact-substance is so high that much of the SO_3 produced is decomposed again into SO_2 and O, or these gases never combine.

The demand for strong and fuming sulphuric acid by the manufacturers of artificial dyestuffs and other organic preparations, having increased rapidly during the last few years, strenuous efforts have again been made to produce the acid by the contact-process, and by rigorous care in purifying the sulphur dioxide and air before they enter the chamber containing the contact-substance, and by careful regulation of the temperature of the latter great success has been attained. Indeed, it is claimed that so much as 96 per cent. of the SO_2 may be converted into SO_3, and there is little reason to doubt that the process will ultimately displace the chamber-process.

Sulphur dioxide is produced in a pyrites burner as in the chamber-process, sufficient air for its conversion into SO_3 being drawn in through the burner. This mixture of gases is then thoroughly washed, dried, and passed into a chamber containing platinised asbestos spread on

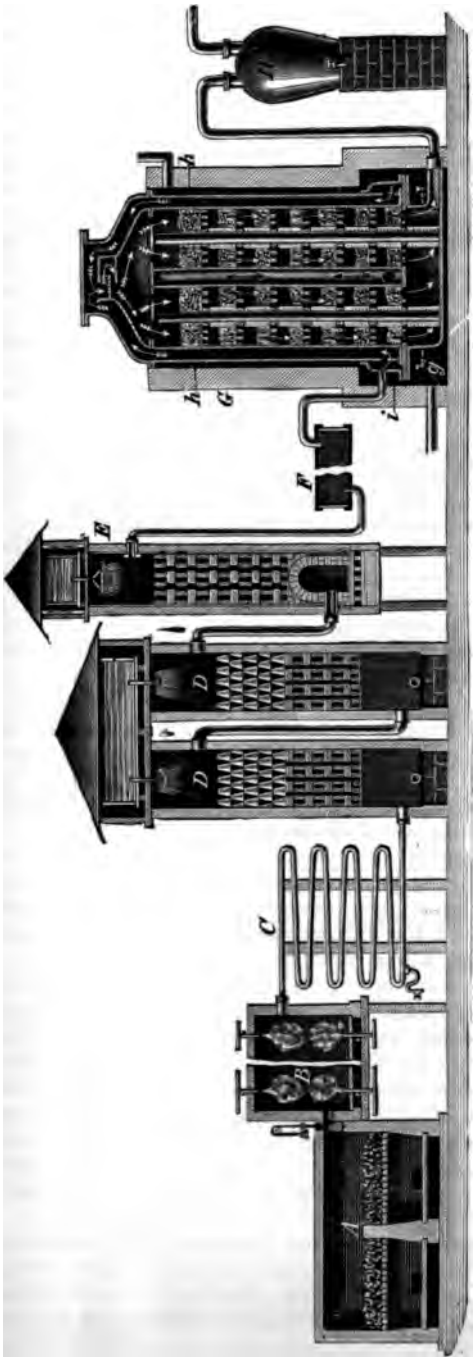


Fig 177.—Contact-process for the manufacture of sulphuric acid.

shelves. At first the chamber must be artificially heated to a temperature of about 250° to 300° C. in order to induce the combination, but after this has once set in, it becomes necessary to withdraw the artificial heat and to circulate the gases which are to be combined, around the contact-chamber in order that they may equalise the temperature therein, and prevent it from rising at any one point to that at which decomposition of the SO_3 occurs. The sulphuric anhydride is finally absorbed in water to produce sulphuric acid.

Fig. 177 illustrates the kind of plant used in the contact-process for the manufacture of sulphuric acid. The gases from the pyrites kiln *A* pass through a dust chamber *B*, where they are submitted to the action of steam jets in order to mix them, and at the same time to dilute the sulphuric acid, which is always produced during the combustion in the pyrites burner, so that afterwards it may not attack the metal of the apparatus. The gases next pass through lead pipes *C*, exposed to the atmosphere, in order to cool them below 100° C., and then up through washing towers *D* supplied with water. As the presence of moisture in the gases leads to formation of H_2SO_4 in the contact-chamber, which damages the platinum, the gases are next

dried in a tower *E* supplied with strong sulphuric acid. To ensure continued activity of the platinum, it is desirable to watch carefully over the purity of the gases entering the contact-chamber; for this purpose they are passed through a long box *F*, having glass ends so that the operative can observe from one end a light burning at the other, and thus determine whether the gases are free from suspended matter. A periodical chemical testing of the gases is also made by passing some of them through water, which is afterwards analysed for arsenic and other impurities.

The contact-chamber *G* (which is drawn to an exaggerated scale for the sake of clearness) contains columns of perforated shelves on which platinised asbestos is spread. At first the chamber is heated by the gas jets *g*, the products of combustion of which pass up the flue *h*. The cold gases being admitted at *i*, and passing around the columns of shelves, become heated by transmission through the walls of the flue and enter the columns, as indicated by the arrows, at a temperature high enough to combine under the influence of the platinum. The gas jets may now be turned off, for the heat of combination is communicated to the gases as they pass around the columns, and the whole apparatus may be maintained at the most favourable temperature for combination, about 350° C.

The SO_3 produced is absorbed by water in a series of vessel like *H*.

No means of circulating the gases is shown in the figure, but this is best effected by pumps.

Properties of oil of vitriol.—The properties of concentrated sulphuric acid are very characteristic. Its great weight (sp. gr. 1.84),* freedom from odour, and oily appearance, distinguish it from any other liquid commonly met with, which is fortunate, because it is difficult to preserve a label upon the bottles of this powerfully corrosive acid. Although, if absolutely pure, it is perfectly colourless, the ordinary acid used in the laboratory has a peculiar grey colour, due to traces of organic matter. Its high boiling-point, 338° C. (640° F.) has been already noticed; it must be added that vapour of H_2SO_4 is not evolved by the ebullition but the products of its dissociation, $H_2O + SO_3$. When acid of 100 per cent. strength is heated it begins to (apparently) boil at 290° C. and loses SO_3 until its strength has fallen to 98 per cent., when both water and SO_3 distil over and condense together in the receiver. The vapour is perfectly transparent in the vessel in which the acid is boiled; as soon as it issues into the air it condenses into voluminous, dense clouds of a most irritating description. Even a drop of the acid evaporated in an open dish will fill a large space with these clouds. Oil of vitriol solidifies when cooled to about − 34° C. (− 30° F.), though pure H_2SO_4 melts at 10°.5 C. (51° F.). Oil of vitriol rapidly corrodes the skin and other organic textures upon which it falls, usually charring or blackening them at the same time. Poured upon a piece of wood the latter speedily assumes a dark brown colour; and if a few lumps of sugar be dissolved in a very little water, and stirred with oil of vitriol, there is a violent action, and a semi-solid black mass is produced. This property of sulphuric acid is turned to account in the manufacture of blacking, in which treacle and oil of vitriol are employed. These effects are to be ascribed to the powerful attraction of oil of vitriol for water. Woody fibre ($C_6H_{10}O_5$) (which composes the bulk of wood, paper, and linen) and sugar ($C_{12}H_{22}O_{11}$), may be regarded, for the purpose of this explanation, as composed of carbon associated with 5 and 11 molecules of water, respectively, and any cause tending to remove the water would tend to eliminate the carbon.

* The acid containing 97.7 per cent. has the highest sp. gr. 1.8413; that of 98 per cent., 1.8412; 99 per cent., 1.8403; 99.47 per cent., 1.8395; 100 per cent., 1.8384.

The great attraction of this acid for water is shown by the high temperature (often exceeding the boiling-point of water) produced on mixing oil of vitriol with water, which renders it necessary to be careful in diluting the acid.

The water should be placed in a jug, and the oil of vitriol poured into it in a thin stream, a glass rod being used to mix the acid with the water as it flows in. Ordinary oil of vitriol becomes turbid when mixed with water, from the separation of lead sulphate (formed from the evaporating pans), which is soluble in the concentrated, but not in the diluted acid, so that if the latter be allowed to stand for a few hours, the lead sulphate settles to the bottom, and the clear acid may be poured off free from lead. Diluted sulphuric acid has a smaller bulk than is occupied by the acid and water before mixing.

The heat evolved on combining one gram-molecule of H_2SO_4 with one gram-molecule of water amounts to 69.7 gram-units. Decreasing quantities of heat are evolved for successive additions of water, until 200 gram-molecules of water have been added.

The heat thus evolved must be regarded as equivalent to a chemical affinity exerted between the acid and water; several compounds of sulphuric acid with water have been crystallised. The most notable of these is $H_2SO_4.H_2O$, corresponding with an acid of sp. gr. 1.78; it is called *dihydrated sulphuric acid* ($SO_3.2H_2O$). in contradistinction to oil of vitriol, which is *monohydrated sulphuric acid* ($SO_3.H_2O$); it solidifies to a mass of ice-like crystals at 8° C., and on this account is called *glacial sulphuric acid*. When sold instead of oil of vitriol it may be recognised by its freezing in winter. The hydrate $H_2SO_4.2H_2O$ corresponds with the maximum contraction which occurs when H_2SO_4 and water are mixed, and with an acid of sp. gr. 1.63; it is called *trihydrated sulphuric acid* or *orthosulphuric acid*.

The so-called "solidified sulphuric acid" is sodium hydrogen sulphate saturated with sulphuric acid.

Even when largely diluted, sulphuric acid corrodes textile fabrics very rapidly, and though the acid be too dilute to appear to injure them at first, it will be found that the water evaporates by degrees, leaving the acid in a more concentrated state, and the fibre is then perfectly rotten. The same result ensues at once on the application of heat; thus, if characters be written on paper with the diluted acid, they will remain invisible until the paper is held to the fire, when the acid will char the paper, and the writing will appear intensely black.

Fig. 178.—Desiccator for drying over oil of vitriol.

If oil of vitriol be left exposed to the air in an open vessel, it very soon increases largely in bulk from the absorption of water, and a flat dish of oil of vitriol under a glass shade (Fig. 178) is frequently employed in the laboratory for drying substances without the assistance of heat. The drying is of course much accelerated by placing the dish on the plate of an air-pump, and exhausting the air from the shade, so as to effect the drying *in vacuo*. It will be remembered also that oil of vitriol is in constant use for drying gases.

At a red heat, the vapour of oil of vitriol is decomposed into water, sulphur dioxide, and oxygen; $H_2SO_4 = H_2O + SO_2 + O$.

When sulphur is boiled with oil of vitriol, the latter gradually dissolves the melted sulphur, converting it into sulphur dioxide—

$$S + 2H_2SO_4 = 3SO_2 + 2H_2O.$$

All ordinary metals are acted upon by concentrated sulphuric acid when heated, except gold and platinum (the latter does not quite escape when long boiled with the acid), the metal being oxidised by one portion of the acid, which is thus converted into sulphur dioxide, the oxide reacting with another part of the sulphuric acid to form a sulphate. Thus, when silver is boiled with strong sulphuric acid, it is converted into silver sulphate, which is soluble in hot water—

$$Ag_2 + 2H_2SO_4 = Ag_2SO_4 + 2H_2O + SO_2.$$

Should the silver contain any gold, this is left behind in the form of a dark powder. Sulphuric acid is extensively employed for the separation or *parting* of silver and gold. This acid is also employed for extracting gold from copper, and when sulphate of copper is manufactured by dissolving that metal in sulphuric acid (see p. 218), large quantities of gold are sometimes extracted from the accumulated residue left undissolved by the acid. If the sulphuric acid contains nitric acid, it dissolves a considerable quantity of gold, which separates again in the form of a purple powder when the acid is diluted with water, the sulphate of gold formed being reduced by the nitrous acid when the solution is diluted.

Some of the uses of sulphuric acid depend upon its specific action on certain organic substances, the nature of which has not yet been clearly explained. Of this kind is the conversion of paper into *vegetable parchment* by immersion in a cool mixture of two measures of oil of vitriol and one measure of water, and subsequent washing. The conversion is not attended by any change in the weight of the paper.

Proof of the composition of sulphuric acid.—10 grams of sulphuric acid are neutralised by 22.7 grams of PbO, when heated, giving off 1.82 grams of H_2O and leaving 30.9 grams of lead sulphate. Hence sulphuric acid contains 2.02 per cent. of H. 10 grams galena (PbS), containing 8.66 Pb and 1.34 S, when converted into lead sulphate ($PbSO_4$) by nitric acid, yield 12.68 grams. Hence 12.68 grams lead sulphate contain 1.34 S and 2.68 O, being the difference between the lead sulphate and the lead sulphide. The 30.9 grams of lead sulphate furnished by 10 grams of sulphuric acid would therefore contain 3.26 S and 65.2 O, so that 100 parts of sulphuric acid contain 2.02 H, 32.6 S, and 65.2 O, which numbers, divided by the atomic weights, give 2 atoms of H, 1 atom of S, and 4 atoms of O. The molecular weight of sulphuric acid cannot be deduced from the sp. gr. of its vapour because it is dissociated into H_2O and SO_3. But it yields with KOH two salts, one containing an atom of K and an atom of H, and the other containing two atoms of K. Hence these salts must be $KHSO_4$ and K_2SO_4, and the molecule of the acid must be H_2SO_4.

135. *Sulphates.*—At common temperatures sulphuric acid displaces all other acids from their salts; many cases will be remembered in which this power of sulphuric acid is turned to account.

So great is the acid energy of sulphuric acid, that when it is allowed to act on an indifferent or acid metallic oxide, it causes the separation of a part of the oxygen, and reacts with the basic oxide so produced. Advantage is sometimes taken of this circumstance for the preparation of oxygen; for instance, when manganese dioxide is heated with sulphuric acid, sulphate of manganese is produced, and oxygen disengaged; $MnO_2 + H_2SO_4 = MnSO_4 + O + H_2O$.

Again, if chromic anhydride be treated in the same way, chromic sulphate will be produced, with liberation of oxygen—

$$2CrO_3 + 3H_2SO_4 = Cr_2.3SO_4 + O_3 + 3H_2O.$$

A mixture of potassium bichromate ($K_2O.2CrO_3$) and sulphuric acid is sometimes used as a source of oxygen.

Sulphuric acid is a *dibasic* acid, that is, it contains two atoms of hydrogen which may be exchanged for a metal. In *normal sulphates*, both atoms of H are so exchanged, as in K_2SO_4, the normal potassium sulphate. When only a part of the H is exchanged, *acid sulphates* are produced; thus $KHSO_4$ is acid potassium sulphate, which is very useful in blowpipe and metallurgic chemistry, because, when heated, it yields normal potassium sulphate and sulphuric acid; $2KHSO_4 = K_2SO_4 + H_2SO_4$. When the two atoms of H in H_2SO_4 are exchanged for different metals, *double sulphates* are formed; potassium alum, $KAl(SO_4)_2$, is an example of this class, in which one-fourth of the H in $2H_2SO_4$ is exchanged for potassium, and the other three atoms by triatomic aluminium.

The following table exhibits the composition of the sulphates most frequently met with:

Chemical Name.	Common Name.	Formula.
Potassium sulphate	Sal polychrest	K_2SO_4
Sodium sulphate	Glauber's salt	$Na_2SO_4.10H_2O$
Hydropotassium sulphate	Bisulphate of potash	$KHSO_4$
Ammonium sulphate		$(NH_4)_2SO_4$
Barium sulphate	Heavy spar	$BaSO_4$
Calcium sulphate	Gypsum	$CaSO_4.2H_2O$
Magnesium sulphate	Epsom salts	$MgSO_4.7H_2O$
Potassium-aluminium sulphate	Potash-alum	$KAl(SO_4)_2.12H_2O$
Ammonium-aluminium sulphate	Ammonia-alum	$NH_4Al(SO_4)_2.12H_2O$
Potassium-chromium sulphate	Chrome-alum	$KCr(SO_4)_2.12H_2O$
Ferrous sulphate	Green vitriol / Copperas	$FeSO_4.7H_2O$
Manganese sulphate		$MnSO_4.5H_2O$
Zinc sulphate	White vitriol	$ZnSO_4.7H_2O$
Lead sulphate		$PbSO_4$
Cupric sulphate	Blue vitriol / Blue stone	$CuSO_4.5H_2O$

In consequence of the tendency of sulphuric acid to break up into sulphur dioxide and oxygen at a high temperature, most of the sulphates are decomposed by heat; cupric sulphate, for example, when very strongly heated, leaves cupric oxide, whilst sulphur dioxide and oxygen escape; $CuSO_4 = CuO + SO_2 + O$. Ferrous sulphate is more easily decomposed, some of the SO_3 escaping decomposition, whilst the remainder breaks up into SO_2 and O, the latter oxidising the ferrous oxide which would otherwise be left; $2FeSO_4 = Fe_2O_3 + SO_2 + SO_3$.

The normal sulphates of potassium, sodium, barium, strontium, calcium, and lead are not decomposed by heat, and sulphate of magnesium is only partly decomposed at a very high temperature.

When a sulphate of an alkali or alkaline earth metal is heated with charcoal, the carbon removes the whole of the oxygen, and a sulphide of the metal remains, thus: K_2SO_4 (*Potassium sulphate*) $+ C_4 = K_2S$ (*Potassium sulphide*) $+ 4CO$. Hydrogen, at a high temperature, effects a similar decomposition.

Even at the ordinary temperature, calcium sulphate in solution is sometimes deoxidised by organic matter; this may occasionally be noticed in well and river waters when kept in closed vessels; they acquire a strong smell of hydrogen sulphide, in consequence of the conversion of a part of the calcium sulphate into sulphide by the organic constituents of the water, and the subsequent decomposition of the calcium sulphide by the carbonic acid present in the water.

Sulphur sesquioxide, S_2O_3, is an unstable, blue, crystalline solid, obtained by the gradual addition of sulphur to sulphuric anhydride in the cold. It dissolves in fuming sulphuric acid to a blue liquid, but is decomposed by water, alcohol, or ether, sulphur being liberated.

Persulphuric anhydride, S_2O_7, is a crystalline compound formed by electrising (p. 65) a mixture of SO_2 and O. It is also produced by the interaction of hydrogen dioxide and H_2SO_4. It is very volatile and unstable, but its solution in fairly concentrated sulphuric acid possesses oxidising properties and probably contains *persulphuric acid* HSO_4 ($?H_2S_2O_8$). Such a solution is formed at the anode during the electrolysis of sulphuric acid of medium strength, and its presence is to be detected in the ordinary lead electric accumulator. The *persulphates* are easily prepared by the electrolysis of solutions of the sulphates in dilute sulphuric acid. To prepare *potassium persulphate*, KSO_4 ($?K_2S_2O_8$), a saturated solution of $KHSO_4$ is contained in a platinum dish, kept cool; a porous pot containing dilute H_2SO_4 is immersed in the solution, and in this a platinum wire is introduced to serve as a cathode; the platinum dish is made the anode. By continuing the electrolysis (current = 2 - 3 ampères) for some time, crystals of KSO_4 are deposited in the dish. When dried and heated they evolve SO_3 and O, K_2SO_4 being left. Barium chloride gives no precipitate with a solution of a persulphate until heated, when the $Ba(SO_4)_2$ decomposes, $BaSO_4$ being precipitated. The persulphates behave as oxidising agents in solution, and find application as bleaching agents, although the use of the ammonium salt as a "reducer" in photography can hardly be explained by reference to its oxidising power.

It has been found that when a persulphate is treated with strong H_2SO_4 the solution rapidly liberates iodine from an iodide, whereas persulphuric acid does so only slowly. Hence such a solution (*Caro's acid*) is supposed to contain another persulphuric acid, to which the formula H_2SO_5 has been given.

Besides the oxyacids of sulphur already described the following are known:—

Sulphurous	H_2SO_3
Sulphuric	H_2SO_4
Thiosulphuric (formerly hyposulphurous)	$H_2S_2O_3$
Hydrosulphurous	$H_2S_2O_4$
Dithionic	$H_2S_2O_6$
Trithionic	$H_2S_3O_6$
Tetrathionic	$H_2S_4O_6$
Pentathionic	$H_2S_5O_6$

136. **Thiosulphuric acid** ($H_2S_2O_3$ or $SO_2.OH.SH$).—This acid has not been obtained in the separate state; but many salts are known which are evidently derived from it, and such salts are called *hyposulphites* or *thiosulphates*.

The *sodium thiosulphate* is by far the most important of these salts, being very largely employed in photography, under the name of hyposulphite, and as a substitute for sodium sulphite as an *antichlore*. The simplest method of preparing it consists in digesting powdered roll sulphur with solution of sodium sulphite (Na_2SO_3), when the latter dissolves an atom of sulphur and becomes thiosulphate ($Na_2S_2O_3$), which crystallises from the solution, when sufficiently evaporated, in fine prismatic crystals, having the formula $Na_2S_2O_3.5H_2O$.

On a large scale, sodium thiosulphate is more economically prepared from the calcium thiosulphate obtained by exposing the refuse (*tank-waste* or *soda-waste*) of the alkali works to the air for some days. This refuse contains a large proportion of calcium sulphide, which becomes converted into thiosulphate by oxidation; $2CaS + O_4 + H_2O = CaS_2O_3 + Ca(OH)_2$.

The thiosulphate is dissolved out by water, and solution mixed with sodium carbonate, when calcium carbonate is precipitated and sodium thiosulphate remains in solution; $CaS_2O_3 + Na_2CO_3 = CaCO_3 + Na_2S_2O_3$.

The most remarkable and useful property of the sodium thiosulphate

is that of dissolving the chloride and iodide of silver, which are insoluble in water and most other liquids; hence its use in photography.

On mixing a solution of silver nitrate with one of sodium chloride, a white precipitate of silver chloride is obtained, the separation of which is promoted by stirring the liquid; $AgNO_3 + NaCl = AgCl + NaNO_3$. The precipitate may be allowed to settle and washed twice or thrice by decantation. One portion of the silver chloride is transferred to another glass, mixed with water, and solution of sodium thiosulphate added by degrees. The silver chloride is very easily dissolved, yielding an intensely sweet solution, which contains the thiosulphate of sodium and silver, produced by double decomposition between the silver chloride and sodium thiosulphate; $2AgCl + 3Na_2S_2O_3 = Ag_2Na_4(S_2O_3)_3 + 2NaCl$. The sodium silver thiosulphate may be obtained in crystals from the solution.

When the silver chloride is acted on by a weaker solution of the thiosulphate, another thiosulphate of sodium and silver is formed, which is very insoluble in water; $AgCl + Na_2S_2O_3 = NaCl + NaAgS_2O_3$. Hence the necessity for using a strong solution of the hyposulphite in fixing photographic prints.

If the other portion of the silver chloride be exposed to the action of light, and especially of direct sunlight, it assumes by degrees a dark slate colour, possibly from the formation of silver subchloride: $4AgCl + H_2O = 2Ag_2Cl + HCl + HOCl$. By treating this darkened silver chloride with the hyposulphite, as before, the unaltered silver chloride will be entirely dissolved, but the subchloride will be decomposed into monochloride, which dissolves in the hyposulphite, and metallic silver, which is left in a very finely divided state as a black powder. The application of these facts in photography is well illustrated by the following experiments: A sheet of paper is soaked for a minute or two in a solution of 10 grains of common salt in an ounce of water contained in a flat dish. It is then dried, and soaked for three minutes in a solution of 50 grains of silver nitrate in an ounce of water. The paper thus becomes impregnated with silver chloride formed by the decomposition between the sodium chloride and the silver nitrate. It is now hung up in a dark place to dry. If a piece of lace, or a fern leaf, or an engraving on thin paper, with well-marked contrast of light and shade, be laid upon a sheet of the prepared paper, pressed down upon it by a plate of glass and exposed for a short time to sunlight, a perfect representation of the object will be obtained, those parts of the sensitive paper to which the light had access having been darkened by the formation of silver subchloride, whilst those parts which were protected from the light remain unchanged.

But if this photographic print were again exposed to the action of light, it would soon be obliterated, the unaltered silver chloride in the white parts being acted on by light in its turn. The print is therefore *fixed* by soaking it for a short time in a saturated solution of sodium thiosulphate, which dissolves the white unaltered silver chloride entirely, and decomposes the subchloride formed by the action of light, leaving the black, finely divided metallic silver in the paper. The print should now be washed for two or three hours in a gentle stream of water, to remove all the silver thiosulphate, when it will be quite permanent.

The power of sodium thiosulphate to dissolve silver chloride has also been turned to account for extracting silver from its ores, in which it is occasionally present in the form of chloride.

The behaviour of solution of sodium thiosulphate with powerful acids explains the circumstance that the thiosulphuric acid has not been isolated, for if the solution be mixed with a little dilute sulphuric or hydrochloric acid, it remains clear for a few seconds, and then becomes suddenly turbid from the separation of sulphur, at the same time evolving a powerful odour of sulphur dioxide; $H_2S_2O_3 = H_2O + S + SO_2$. This disposition of the thiosulphuric acid to break up into sulphur dioxide and sulphur also explains the precipitation of metallic sulphides, which often occurs when sodium thiosulphate is added to the acid solutions of the metals. Thus, if an acid solution of antimonious chloride (obtained by boiling crude antimony ore (Sb_2S_3) with hydrochloric acid) be added to a boiling solution of sodium thiosulphate, the sulphur,

separated from the thiosulphuric acid, combines with the antimony to form a fine orange-red precipitate of antimonious sulphide (Sb_2S_3), which is used in painting under the name of *antimony vermilion*. On the large scale, the solution of calcium thiosulphate obtained from the alkali waste is employed in the preparation of antimony vermilion, as being less expensive than the sodium-salt. Lead thiosulphate dissolved in sodium thiosulphate is used as a hair-dye, depositing the black lead sulphide.

A solution of sodium thiosulphate bleaches iodine solution, becoming changed into a solution of sodium tetrathionate; $2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$.

When crystals of sodium thiosulphate are heated in the air, they first fuse in their water of crystallisation, then dry up to a white mass, which burns with a blue flame, leaving a residue of sodium sulphate. If heated out of contact with air, sodium pentasulphide will be left with the sodium sulphate; $4(Na_2S_2O_3.5H_2O) = 20H_2O + 3Na_2SO_4 + Na_2S_5$.

Some of the reactions of sodium thiosulphate become more intelligible when the salt is represented as sodium sulphate, $SO_2(ONa)_2$, in which an atom of sulphur has displaced an atom of oxygen, $SO_2.ONa.SNa$.

Hydrosulphurous acid ($H_2S_2O_4$).—In an aqueous solution of sulphurous acid zinc dissolves, forming a yellow solution, without the usual evolution of hydrogen; the solution contains zinc hydrosulphite; $2H_2SO_3 + Zn = ZnS_2O_4 + 2H_2O$.

The solution bleaches organic colours, even Prussian blue, and reduces the salts of silver, mercury, and copper to the metallic state; it is used in the indigo vat for reducing the indigo. It is very unstable, soon becoming colourless zinc sulphite; $ZnS_2O_4 + O + H_2O = ZnSO_3 + H_2SO_3$.

The *sodium salt*, $Na_2S_2O_4$, is obtained by digesting zinc in solution of $NaHSO_3$; $2NaHSO_3 + Zn = Na_2S_2O_4 + Zn(OH)_2$. It forms needle-like crystals very soluble in water, insoluble in strong alcohol, and becoming $NaHSO_3$, by absorption of oxygen from the air. By decomposing the sodium hydrosulphite with oxalic acid, $H_2S_2O_4$ is obtained as an orange-yellow unstable liquid.

137. **Dithionic acid**, or **hyposulphuric acid** ($H_2S_2O_6$), has not at present acquired any practical importance. To prepare a solution of the acid, manganese dioxide in a state of fine division is suspended in water and exposed to a current of sulphur dioxide, the water being kept very cold whilst the gas is passing. A solution of manganese dithionate is thus obtained; $2SO_2 + MnO_2 = MnS_2O_6$. Some manganese sulphate is always formed at the same time; $SO_2 + MnO_2 = MnSO_4$, and if the temperature be allowed to rise, this will be produced in large quantity.

The solution containing the sulphate and dithionate is decomposed by solution of baryta (baryta-water), when manganous oxide is precipitated, together with barium sulphate, and barium dithionate is left in solution. To the filtered solution dilute sulphuric acid is carefully added until all the barium is precipitated as $BaSO_4$, when the solution of dithionic acid is filtered and evaporated *in vacuo* over oil of vitriol. It is a colourless, inodorous liquid, which is decomposed, when heated, into sulphuric acid and sulphur dioxide; $H_2S_2O_6 = H_2SO_4 + SO_2$. Oxidising agents ($HNO_3$, Cl, &c.) convert it into H_2SO_4.

The dithionates are not of any practical importance; they are all soluble, and are decomposed by heat, leaving sulphates, and evolving sulphur dioxide. They are distinguished from the thiosulphates in that they evolve SO_2 when heated with HCl, without depositing sulphur.

138. **Trithionic acid** ($H_2S_3O_6$) is also a practically unimportant acid. It is prepared from the potassium trithionate which is formed by boiling a strong solution of potassium bisulphite with sulphur until the solution becomes colourless, and filtering the hot solution from any undissolved sulphur; $6KHSO_3 + S = 2K_2S_3O_6 + K_2SO_3 + 3H_2O$. The solution deposits potassium trithionate in prismatic crystals. By dissolving these in water, and decomposing the solution with perchloric acid, the potassium is precipitated as perchlorate, and a solution of trithionic acid is produced, from which the acid has been obtained in crystals. It is, however, very unstable, being easily resolved into sulphur dioxide, sulphuric acid, and free sulphur; $H_2S_3O_6 = H_2SO_4 + SO_2 + S$.

139. **Tetrathionic acid** ($H_2S_4O_6$) is rather more stable than the preceding acid,

though equally devoid of practical importance. It is formed when barium thiosulphate, suspended in a little water, is treated with iodine, when the tetrathionate is obtained in crystals; $2(BaS_2O_3)+I_2=BaI_2+BaS_4O_6$. (Compare the action of iodine on sodium thiosulphate, p. 237.) By exactly precipitating the barium from a solution of BaS_4O_6 by dilute H_2SO_4, a solution of tetrathionic acid may be obtained. When boiled, it is decomposed into sulphuric acid, sulphur dioxide, and free sulphur; $H_2S_4O_6=H_2SO_4+SO_2+S_2$.

When solution of ferric chloride is added to sodium thiosulphate, a fine purple colour is at first produced, which speedily vanishes, leaving a colourless solution. The purple colour appears to be due to the formation of the ferric thiosulphate which speedily decomposes, the ultimate result being expressed by the equation $Fe_2Cl_6+2(Na_2S_2O_3)=Na_2S_4O_6+2FeCl_2+2NaCl$.

140. **Pentathionic acid** ($H_2S_5O_6$) possesses some interest as resulting from the action of hydrogen sulphide upon sulphurous acid, when much sulphur is deposited, and pentathionic acid remains in solution: $5H_2S+5H_2SO_3=H_2S_5O_6+9H_2O+S_5$. Besides pentathionic acid, a colliodal form of sulphur, sulphuric acid, tetrathionic acid and hexathionic acid (?) are found in the solution. To obtain a concentrated solution of the acid, H_2S and SO_2 are passed alternately through the same portion, of water until a large deposition of sulphur has occurred. This is allowed some hours to settle; the clear liquid poured off and the solution concentrated by evaporation, first over a water-bath, and finally, *in vacuo*, over oil of vitriol; for a concentrated solution of pentathionic acid is decomposed by heat into H_2SO_4 and SO_2, with separation of sulphur; $H_2S_5O_6=H_2SO_4+SO_2+S_3$.

Bisulphide of Carbon, or Carbon Disulphide.

$CS_2=76$ parts by weight.

141. This very important compound (also called *bisulphuret of carbon*) is found in small quantity among the products of destructive distillation of coal, and is very largely manufactured for use as a solvent for sulphur, phosphorus, caoutchouc, fatty matters, &c. It is one of the few compounds of carbon which can be obtained by the direct union of their elements, and is prepared by passing vapour of sulphur over charcoal heated to redness. The combination is probably endothermic.

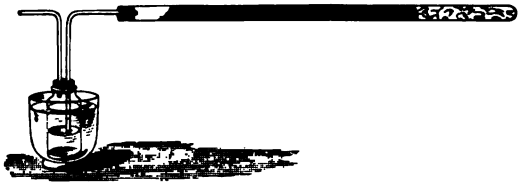


Fig. 179.

In small quantity carbon disulphide is easily prepared in a tube of German glass (combustion-tube) about two feet long and half an inch in diameter (Fig. 179).

This tube is closed at one end, and a few fragments of sulphur dropped into it so as to occupy two or three inches. The rest of the tube is filled up with small fragments of recently calcined wood charcoal. The tube is placed in a combustion-furnace, and its open end connected by a perforated cork with a glass tube, which dips just below the surface of water contained in a bottle placed in a vessel of very cold water. The part of the tube which contains the charcoal is heated first, and when it is red-hot the end containing the sulphur is heated, so that the vapour of sulphur may be slowly passed over the red-hot charcoal. The disulphide being insoluble in water, and much heavier (sp. gr. 1.2 at 0° C.), is deposited beneath the water in the receiver. To purify it from the water and the excess of sulphur which is deposited with it, the water is carefully drawn off with a small siphon, the CS_2 transferred to a flask, and a few fragments of calcium chloride dropped into it to absorb the water. A condenser is attached to the flask (Fig. 180) by a perforated cork, and the flask is gently heated in a water-bath, when the CS_2 is distilled over as a perfectly colourless liquid. The inflammability of the disulphide renders great care necessary.

On a large scale, a fire-clay or cast-iron retort is filled with fragments of charcoal and heated to redness, pieces of sulphur being occasionally dropped in through an earthenware tube passing to the bottom of the retort. When very large quantities are made, coke is employed, and the vapour of sulphur is obtained from iron pyrites. The carbon disulphide is possessed of some very remarkable properties: it is a very brilliant liquid, the light passing through which at certain angles is partly decomposed into its component coloured rays before it reaches the eye. These properties are dependent upon its high refractive and dispersive powers, which are turned to great advantage in optical experiments, especially in *spectrum analysis*, where the rays emanating from a coloured flame are analysed by passing them through a prismatic bottle filled with carbon disulphide. It is also highly *diathermic*, that is, it allows rays of heat to pass through it with comparatively little loss, so that if it be rendered opaque to light by dissolving iodine in it, the rays of light emanating from a luminous object may be arrested, whilst the calorific rays are allowed to pass. Carbon disulphide is a very volatile liquid, readily assuming the form of vapour at the ordinary temperature, and boiling at 46° C. Its vapour, when diluted with air, has a very disgusting and exaggerated odour of sulphuretted hydrogen, but the smell at the mouth of the bottle is ethereal and not unpleasant if the disulphide has been carefully purified.

Fig. 180.

The rapid evaporation of carbon disulphide is, of course, productive of great cold. If a few drops be placed in a watch-glass and blown upon, they soon pass off in vapour, and the temperature of the glass is so reduced that some of the disulphide is frozen;* this melts when the glass is placed in the palm of the hand. If a glass plate be covered with water, a watch-glass containing carbon disulphide placed on it, and evaporation promoted by blowing through a tube, the watch-glass will be frozen on to the plate, so that the latter may be lifted up by it.

The carbon disulphide is exceedingly inflammable; it takes fire at a temperature far below that required to inflame ordinary combustible bodies, and burns with a bright blue flame, producing carbon dioxide and sulphur dioxide ($CS_2 + O_6 = CO_2 + 2SO_2$), and having a great tendency to deposit sulphur unless the supply of air be very good.

If a little carbon disulphide be dropped into a small beaker, it may be inflamed by holding in its vapour a test-tube containing oil heated to about 300° F. (149° C.), which will be found incapable of firing gunpowder or of inflaming any ordinary combustible substance.

The abundance of sulphur separated in the flame of carbon disulphide enables it to burn iron by converting it into sulphide. If some carbon disulphide be boiled in a test-tube provided with a piece of glass tube from which the vapour may be burnt, and a piece of thin iron wire be held in the flame (Fig. 181), it will burn with vivid scintillation, the fusible ferrous sulphide dropping off.

Carbon disulphide is endothermic (p. 96), 76 grams of the liquid absorbing 19,610 gram units in its formation; like most other endothermic gases (C_2H_2, C_2N_2, N_2O, &c.), it may be suddenly decomposed into its elements by a violent shock. This

* This solid matter is probably a cryohydrate of CS_2. Dry CS_2 melts at −113° C.

experiment is performed by detonating 0.05 gram of mercuric fulminate, by means of an electric spark, in an inclined tube open at one end, in which a paper saturated with carbon disulphide has been suspended. After the explosion the carbon and sulphur are seen deposited on the walls of the tube.

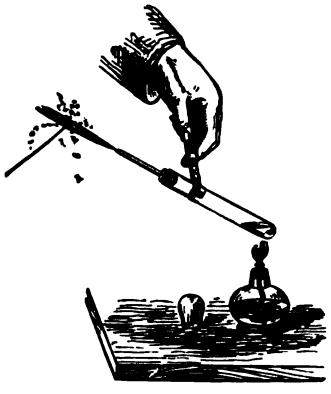


Fig. 181.

The vapour of carbon disulphide acts very injuriously if breathed for any length of time, producing symptoms somewhat resembling those caused by sulphuretted hydrogen. Its poisonous properties have been turned to account for killing insects in grain without injuring the grain.

The chief application of carbon disulphide depends upon its power of dissolving the oils and fats. After as much oil as possible has been extracted from seeds and fruits by pressure, a fresh quantity is obtained by treating the pressed cake with carbon disulphide, which is afterwards recovered by distillation from the oil. In Algiers it is employed for extracting the essential oils in which reside the perfumes of roses, jasmine, lavender, &c.

Carbon disulphide has often been made a starting-point in the attempts to produce organic compounds by synthesis. It may be employed in the formation of the hydrocarbons which are usually derived from organic sources; for if it be mixed with hydrogen sulphide (by passing that gas through a bottle containing the disulphide gently warmed), and passed over copper-turnings heated to redness in a porcelain tube, olefiant gas will be produced; $2CS_2 + 2H_2S + Cu_6 = 6CuS + C_2H_4$. Marsh gas may be obtained in the same way. When passed through a red hot tube the vapour of CS_2 is decomposed into C and S.

The action of carbon disulphide upon ammonia is practically important for the easy production of *ammonium sulphocyanide*, which is formed when the disulphide is dissolved in alcohol, and acted on by ammonia with the aid of heat; $CS_2 + 2NH_3 = H_2S + NH_4CNS$.

Carbon disulphide is often called sulphocarbonic or thiocarbonic anhydride to emphasise its analogy to carbonic anhydride; it combines with some of the sulphur-bases to form *sulphocarbonates* or *thiocarbonates*, which correspond with the carbonates, containing sulphur in place of oxygen. Thus, when a solution of potassium sulphide is mixed with an excess of carbon disulphide, potassium thiocarbonate is obtained in orange-yellow crystals. Even the hydrogen compound corresponding in composition with the unknown H_2CO_3 may be obtained as a yellow oily liquid by decomposing potassium thiocarbonate with hydrochloric acid; $K_2CS_3 + 2HCl = H_2CS_3 + 2KCl$. Potassium thiocarbonate is applied for the destruction of the phylloxera insect which infests vines. As would be expected, the thiocarbonates, when boiled with water, exchange their sulphur for oxygen, becoming carbonates; $K_2CS_3 + 3H_2O = K_2CO_3 + 3H_2S$.

Small quantities of CS_2 may be identified by dissolving in alcoholic potash and adding cupric sulphate, which gives a yellow precipitate of *cuprous xanthate*, $Cu_2S.CS.OC_2H_5$.

The carbon disulphide vapour in coal gas is one of the most injurious of the impurities, and one of the most difficult to remove with economy.

It is especially injurious, because, when burning in the presence of aqueous vapour, a part of its sulphur is converted into sulphuric acid, the corrosive effects of which are so damaging. Several processes have been devised for its removal, but that which is now almost universally adopted consists in absorbing it in lime which has already become saturated with H_2S in the course of the purification of the gas, and thus contains calcium hydrosulphide, $Ca(SH)_2$. This compound combines with the CS_2 to form calcium thiocarbonate, $Ca(SH)_2 + CS_2 = CaCS_3 + H_2S$.

Carbon monosulphide, CS, is deposited when CS_2 is exposed to sunlight, or left for some weeks in contact with iron wire; $2CS_2 + Fe = FeS_2 + 2CS$. The FeS_2 is dissolved out by HCl, leaving the CS as a red-brown powder, of sp. gr. 1.66, insoluble in alcohol and benzene, slightly soluble in hot ether and CS_2. It is soluble in boiling nitric acid and in boiling strong potash. At about 200° C. it is decomposed into carbon, sulphur, and a little disulphide. It is converted into the latter by heating with excess of sulphur.

Tricarbon disulphide, C_3S_2, has been obtained by boiling CS_2 in a flask, the upper portion of which contains an electric arc, and condensing the vapour, after it has been thus heated, so that it may fall back into the flask. It is a deep red liquid (sp. gr. 1.27) which has a very irritating odour. When heated it is changed to a black mass of the same percentage composition.

Carbon Oxysulphide (COS = 60 parts by weight = 2 volumes).—This compound, which may be regarded as CO_2 in which S has been substituted for O, is formed when a mixture of carbonic oxide with sulphur vapour is acted on by electric sparks, or passed through a red-hot porcelain tube; also when carbon disulphide vapour is passed over white-hot clay, and when CdS is heated in $COCl_2$.

It is easily prepared by gently heating potassium sulphocyanide, KCNS, with oil of vitriol diluted with four-fifths of its volume of water, and collecting the gas over mercury. The action of the sulphuric acid upon the sulphocyanide produces hydrosulphocyanic acid; $KCNS + H_2SO_4 = HCNS + KHSO_4$; which is then decomposed by the water in the presence of the excess of sulphuric acid, into COS and NH_3, the latter combining with the sulphuric acid; $HCNS + H_2O = NH_3 + COS$. The gas has a peculiar, disagreeable odour, recalling that of carbon disulphide; it is more than twice as heavy as air (sp. gr. 2.11), and is very inflammable, burning with a blue flame, and yielding CO_2 and SO_2. Potash absorbs and decomposes it, yielding carbonate and sulphide of potassium; $COS + 4KOH = K_2S + K_2CO_3 + 2H_2O$. Ammonia absorbs it freely, and, on evaporation, evolves H_2S and deposits crystals of urea; $COS + 2NH_3 = H_2S + CO(NH_2)_2$.

141. *Nitrogen tetrasulphide* (N_4S_4) is produced when chloride of sulphur, dissolved in benzene, is acted on by gaseous ammonia, $16NH_3 + 6S_2Cl_2 = 12NH_4Cl + N_4S_4 + S_8$. The precipitate obtained is washed with water to remove NH_4Cl and is then fractionally crystallised from CS_2 to separate the N_4S_4 and S, the latter being the more soluble. This substance melts at 178° C. and is remarkable for its sparing solubility, its irritating odour, and its explosibility when struck or sharply heated, its elements being held together by a very feeble attraction.

Nitrogen pentasulphide, N_2S_5, is a red oil obtained by heating the tetrasulphide, dissolved in CS_2, in a sealed tube at 100° C., distilling the CS_2 and extracting the residue with ether which leaves the N_2S_5 on evaporation. Its sp. gr. is 1.9 and it melts at 10° C. It resembles iodine in odour and burns the skin.

142. **Chlorides of Sulphur.**—The *subchloride*, or *sulphur monochloride* ($S_2Cl_2 = 135$ parts by weight), is the most important of these, since it is employed in the process of vulcanising caoutchouc. It is very easily prepared by passing dry chlorine over sulphur very gently heated in a retort (Fig. 182); the sulphur quickly melts, and the sulphur monochloride distils over into the receiver as a yellow volatile liquid, boiling at 280° F. (138° C.), which has a most peculiar odour. It fumes strongly in air, the moisture decomposing it, forming hydrochloric and sulphurous acids, and causing a deposit of sulphur upon the neck of the bottle; $2S_2Cl_2 + 3HOH = 4HCl + SO(OH)_2 + S_3$.

When poured into water it sinks (sp. gr. 1.68) and slowly decomposes;

the solution contains, beside hydrochloric and sulphurous acids, some of the acids containing a larger proportion of sulphur. If phosphorus dissolved in carbon disulphide be mixed with sulphur monochloride, the liquid will take fire on addition of ammonia. The specific gravity of the vapour of S_2Cl_2 is 4.7, showing that it is 68 times as heavy as hydrogen and therefore cannot have the formula SCl.

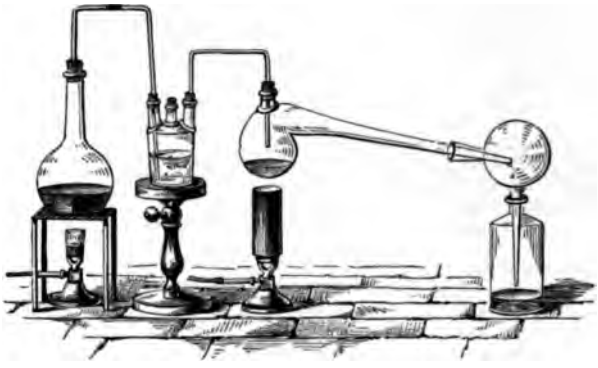


Fig. 182.—Preparation of sulphur monochloride.

Sulphur dichloride (SCl_2) is a far less stable compound than the preceding chloride, from which it is obtained by the action of an excess of chlorine. It is a dark-red fuming liquid, easily resolved, even by sunlight, into free chlorine and sulphur monochloride. *Sulphur tetrachloride* (SCl_4) has also been obtained.

Corresponding bromides and iodides of sulphur are known. Of these the *di-iodide* (SI_2) is a crystalline unstable substance, produced by the direct union of its elements, and occasionally employed in veterinary medicine under the name of *black sulphur*.

SELENIUM.

Se = 78.5 parts by weight.

143. Selenium (Σελήνη, the moon) is a rare element, very closely allied to sulphur in its natural history, physical characters, and chemical relations to other bodies. It is found sparingly in the free state associated with some varieties of native sulphur, but more commonly in combination with metals, forming *selenides*, which are found together with the sulphides. The iron pyrites of Fahlun, in Sweden, is especially remarkable for the presence of selenium, and was the source whence this element was first obtained. The Fahlun pyrites is employed for the manufacture of oil of vitriol, and in the leaden chambers a reddish-brown deposit is found, which was analysed by Berzelius in 1817, and found to contain the new element.

In order to extract selenium from the seleniferous deposit of the vitriol works this may be boiled with sulphuric acid diluted with an equal volume of water, and nitric acid added in small portions until the oxidation is completed, when no more red fumes will escape. The solution, containing selenious and selenic acids, is largely diluted with water, filtered from the undissolved matters, mixed with about one-fourth of its bulk of hydrochloric acid, and somewhat concentrated by evaporation, when the hydrochloric acid reduces the selenic to selenious acid—

$$H_2SeO_4 + 2HCl = H_2SeO_3 + H_2O + Cl_2.$$

A current of sulphurous acid gas is now passed through the solution, when the selenium is precipitated in fine red flakes, which collect into a dense black mass when the liquid is gently heated; $H_2SeO_3 + H_2O + 2SO_2 = 2H_2SO_4 + Se$.

The proportion of selenium in the deposit from the leaden chambers is variable. The author has obtained 3 per cent. by this process.

Like sulphur, selenium exists in an amorphous and a crystalline form, and more than one of the latter appear to exist. *Amorphous* selenium is the red precipitate formed by precipitating the element, either as described above or by adding an acid to a solution of it in potassium cyanide. When kept at 100° C. for some time this form of selenium suddenly changes into the grey crystalline variety with much evolution of heat. Amorphous selenium has sp. gr. 4.26 and is soluble in CS_2; it becomes plastic a little above 100° C. and if melted and cooled quickly it forms a vitreous mass (sp. gr. 4.28), still amorphous, but if carefully cooled so that it may superfuse it solidifies to the grey crystalline form (sp. gr. 4.8); but when less carefully cooled it solidifies to a mass of red monoclinic prisms isomorphous with monoclinic sulphur and of sp. gr. 4.47. These crystalline forms are insoluble in CS_2.

Amorphous and monoclinic selenium are very poor conductors of electricity, but the grey crystalline form is a fair conductor and a better one in light than in darkness, a property which is applied in apparatus for seeing at a distance.

Selenium boils at 680° C. and its vapour shows much the same variation in density as that exhibited by sulphur.

Selenium is less combustible than sulphur; when heated in air it burns with a blue flame, and emits a peculiar odour like that of putrid horse-radish, which appears to be due to the formation of a little selenietted hydrogen from the moisture of the air. The odour serves for the detection of selenium compounds when they are heated on charcoal. When heated with oil of vitriol, selenium forms a green solution which deposits the selenium again when poured into water.

Selenium dioxide (SeO_2), corresponding with sulphur dioxide, is the product of combustion of selenium in oxygen. It is best obtained by dissolving selenium in boiling nitric acid (which would convert sulphur into sulphuric acid), and evaporating to dryness, when the selenium dioxide remains as a white solid which sublimes in needle-like crystals when heated. When dissolved in boiling water it yields crystalline *selenious acid*, $SeO(OH)_2$.

Selenic acid (H_2SeO_4 or $SeO_2(OH)_2$).—Potassium selenate is formed when selenium is oxidised by fused nitre; $2KNO_3 + Se = K_2SeO_4 + 2NO$. By dissolving the potassium selenate in water, and adding lead nitrate, a precipitate of lead selenate ($PbSeO_4$) is obtained, and if this be suspended in water and decomposed by passing hydrosulphuric acid gas, lead will be removed as insoluble sulphide, and a solution of selenic acid will be obtained: $PbSeO_4 + H_2S = H_2SeO_4 + PbS$. This solution may be evaporated till it has a sp. gr. of 2.6 (when it very closely resembles oil of vitriol) and heated in a vacuum at 180° C. so long as any distils over; the residue will crystallise on cooling. The crystals (sp. gr. 2.95) melt at 58° C. and are deliquescent;-the hydrate, $H_2SeO_4.H_2O$, melts at 25° C. It is decomposed at 260° C. into H_2O, SeO_2, and O. It oxidises the metals as oil of vitriol does, and even dissolves gold. The selenates closely resemble the sulphates, but they are decomposed when heated with hydrochloric acid, chlorine being evolved and selenious acid produced.

Hydroselenic acid, or *selenietted hydrogen* (H_2Se), is the analogue of sulphuretted hydrogen, and is produced by a similar process. It is even more offensive and poisonous than that gas, and acts in a similar way upon metallic solutions, precipitating the *selenides*.

There are two *chlorides of selenium:* the monochloride, Se_2Cl_2, a brown volatile liquid corresponding with sulphur monochloride; and the tetrachloride, $SeCl_4$, a white crystalline solid. $SeOCl_2$ is also known.

Notwithstanding the resemblance between the two elements, *sulphides of selenium* are known, probably SeS_2 and SeS_3. The former is obtained as a yellow precipitate when hydrogen sulphide is passed into solution of selenious acid.

TELLURIUM.

Te = 126 parts by weight.

144. Tellurium (from *tellus*, the earth) is connected with selenium by analogies stronger than those which connect that element with sulphur. It is even less frequently met with than selenium, being found chiefly in certain Transylvanian gold ores. It occasionally occurs in an uncombined form, but more frequently in combination with metals. It has recently been found in Colorado, masses of native tellurium up to 12 kilos. in weight having been met with; also *coloradoite*,

or murcuric telluride, HgTe. Bismuth telluride, or *tetradymite*, Bi_2Te_3, has been found in California, and lead telluride, or *altaite*, in North Carolina. *Foliated* or *graphic tellurium*, or *sylvanite*, is a black material containing the tellurides of silver and gold. Arsenical pyrites sometimes contains tellurium, apparently as TeS_2.

Tellurium is extracted from the foliated ore by a process similar to that for obtaining selenium. From bismuth telluride it is procured by strongly heating the ore with a mixture of potassium carbonate and charcoal, when potassium telluride is formed, which dissolves in water to a purple-red solution, wherefrom tellurium is deposited on exposure to air; $K_2Te + O + H_2O = 2KOH + Te$. It is purified by sublimation in hydrogen when it is deposited as white lustrous hexagonal rhombohedra, isomorphous with S and Se.

Considerable quantities of tellurium are now obtainable from the sludge deposited in the electrolytic cells in which copper is refined, the crude metal having collected the tellurium contained in the original ore.

Tellurium much more nearly resembles the metals than the non-metals in its physical properties (sp. gr. 6.2), and is on that account often classed among the former, but it is not capable of forming a true basic oxide. In appearance it is very similar to bismuth (with which it is so frequently found), having a pinkish metallic lustre, and being, like that metal, crystalline and brittle. When precipitated it is a black amorphous powder, which becomes crystalline, with evolution of much heat, when warmed. It fuses at 455° C. and boils, yielding a yellow vapour, of normal vapour density, at 1390° C. When heated in air it burns with a blue flame edged with green, and emits fumes of tellurium dioxide (TeO_2) and a peculiar odour.

Like selenium, tellurium is dissolved by strong sulphuric acid, yielding a purple-red solution, from which water precipitates it unchanged.

The *oxides of tellurium* correspond in composition with those of sulphur. *Tellurous acid* (H_2TeO_3) is precipitated when a solution of tellurium in dilute nitric acid is poured into water. If the nitric solution is boiled, a crystalline precipitate of tellurous anhydride, TeO_2, is obtained, but when the solution is evaporated a well crystallised basic nitrate, $Te_2O_3(OH)NO_3$, separates. Unlike selenious acid tellurous acid is sparingly soluble in water. The anhydride is easily fusible, forming a yellow glass, which becomes white on cooling, and may be sublimed unchanged. Tellurous acid is rather a feeble acid, and with some of the stronger acids the anhydride forms soluble compounds in which it takes the part of a very feeble base.

Telluric acid (H_2TeO_4) is also a feeble acid obtained by oxidising tellurium with nitre, precipitating the potassium tellurate with barium chloride, and decomposing the barium tellurate with sulphuric acid. On evaporating the solution, crystals of telluric acid ($H_2TeO_4.2H_2O$) are obtained, which become H_2TeO_4 at a moderate heat, and when heated nearly to redness are converted into an orange-yellow powder, which is the anhydride, TeO_3. In this state it is insoluble in acids and alkalies. When strongly heated it evolves oxygen, and becomes tellurous anhydride. The tellurates are unstable salts which are converted into tellurites when heated. Solutions of alkali tellurates yield a precipitate of tellurium when boiled with alkali carbonates and glucose.

Telluretted hydrogen or *hydrotelluric acid* (H_2Te) exhibits in the strongest manner the chemical analogy of tellurium with selenium and sulphur. It is a gas of dreadful odour and similar to H_2S in most of its properties. When its aqueous solution is exposed to the air, it yields a brown deposit of tellurium. When passed into metallic solutions it precipitates the tellurides. The gas is prepared by decomposing telluride of zinc with hydrochloric acid.

The most characteristic property of tellurium compounds is that of furnishing the purple solution of potassium telluride when fused with potassium carbonate and charcoal, and treated with water; in the total absence of oxygen, however, the solution is colourless. Two solid *chlorides of tellurium* have been obtained; $TeCl_2$ is a black solid with a violet-coloured vapour, and is decomposed by water into tellurium and $TeCl_4$. The latter may be obtained as a white crystalline volatile solid, decomposed, by much water, into hydrochloric and tellurous acids.

145. Review of the sulphur group of elements.—The three divalent elements—sulphur, selenium, and tellurium—exhibit a relation of a similar character to that observed between the members of the chlorine group, both in their physical and chemical properties.

Sulphur is a pale yellow solid, easily fusible and volatile, without any trace of metallic lustre, and of sp. gr. 2.05, melting at 118° and boiling at 444° C. Selenium is either a red powder or a lustrous mass appearing black, but transmitting red light through thin layers, of specific gravity 4.8, melting-point 217° C., and boiling-point 680° C. Tellurium has a brilliant metallic lustre, sp. gr. 6.2, melting-point 455° C., and boiling-point 1390° C.

Sulphur (atomic weight 32) has the most powerful attraction for oxygen, hydrogen, and the metals. Selenium (atomic weight 79) ranks next in the order of chemical energy. Tellurium (atomic weight 126.5) has a less powerful attraction for oxygen, hydrogen, and the metals, than either sulphur or selenium has. This element appears to stand on neutral ground between the non-metallic bodies and the less electro-positive metals.

BORON.

B‴ = 11 parts by weight.

This element resembles carbon in several respects, but is not properly classed therewith because it is of the trivalent type, while carbon is tetravalent. The element itself does not possess much importance; it is found only in combination with oxygen in the mineral world, whence very small quantities find their way into some plants such as the grape-vine and into sea-water. The oxide will be considered first.

Boric anhydride, or *Anhydrous Boric Acid* ($B_2O_3 = 69.8$ parts by weight).—A saline substance called *borax* ($Na_2B_4O_7.10Aq$) has long been used in medicine, in working metals, and in making imitations of precious stones; this substance was originally imported from India and Thibet, where it was obtained in crystals from the waters of certain lakes, and came into this country under the native name of *tincal*, consisting of impure borax, surrounded with a peculiar soapy substance. Borax has recently been found in abundance in the bed of a dried-up lake in the Sierra Nevada.

In 1702, in the course of one of those experiments to which, though empirical in their nature, scientific chemistry is now so deeply indebted, Homberg happened to distil a mixture of borax and green vitriol (ferrous sulphate), when he obtained a new substance in pearly plates, which was found useful in medicine, and received the name of *sedative salt*. A quarter of a century later Lemery found that this substance might be separated from borax by employing sulphuric acid instead of ferrous sulphate, and that it possessed acid properties, whence it was called *boracic* acid, now abbreviated to *boric* acid.

Much more recently this acid has been obtained in a free state from natural sources, and is now largely imported into this country from the volcanic districts in the north of Italy, where it issues from the earth in the form of vapour, accompanied by violent jets of steam, which are known in the neighbourhood as *soffioni*. It would appear easy enough, by adopting arrangements for the condensation of this steam, to obtain the *boric* acid which accompanies it, but it is found necessary to cause the steam to deposit its boric acid by passing it through water, for which purpose basins of brickwork (*lagunes*, Fig. 183) are built up around the soffioni, and are kept filled with water from the neighbouring

springs or brooks; this water is allowed to flow successively into the different lagunes, which are built upon a declivity for that purpose, and it thus becomes impregnated with about 1 per cent. of boric acid. The necessity for expelling a large proportion of this water, in order to obtain the boric acid in crystals, formed for a long time a great obstacle to the success of this branch of industry in a country where fuel is very expensive. In 1817, however, Larderello conceived the project of evaporating this water by the steam-heat afforded by the soffioni themselves, and several hundred tons of boric acid are now annually produced in this manner. The evaporation is conducted in shallow leaden evaporating pans (A, Fig. 183), under which the steam from the soffioni is conducted through the flues (F) constructed for that purpose. As the demand for boric acid increased on account of the immense consumption of borax in the porcelain manufacture, the experiment was made, with success, of boring into the volcanic strata, and thus producing artificial soffioni, yielding boric acid.

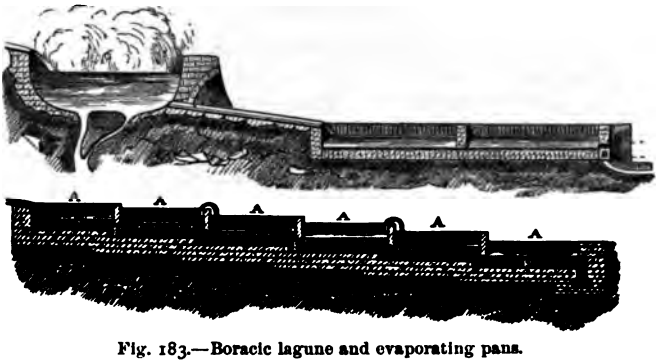


Fig. 183.—Boracic lagune and evaporating pans.

The crystals of boric acid, as imported from these sources, contain salts of ammonia and other impurities. They dissolve in about three times their weight of boiling water, and crystallise on cooling, since they require 26 parts of cold water to dissolve them. These crystals have the sp. gr. 1·435 and are represented by the formula $3H_2O.B_2O_3$ (or H_3BO_3, or $B(OH)_3$). If they are sharply heated in a retort they partly distil unchanged, together with the water derived from the decomposition of another part; but if they be not heated above 212° F., they effloresce and become $H_2O.B_2O_3$.* When heated for a long time to 140° C. this becomes $H_2O.2B_2O_3$, sometimes written $H_2B_4O_7$, and called *pyroboric acid*, whilst $H_2O.B_2O_3$ is HBO_2, *metaboric acid*, and the crystals, H_3BO_3, are *orthoboric acid*. When pyroboric acid is heated further the whole of the water passes off, carrying with it a little boric acid, and the B_2O_3 fuses to a glass, which remains perfectly transparent on cooling (*vitreous boric acid*). This is slowly volatilised by the continued action of a very high temperature. It dissolves very slowly in water. Boric acid is an *antiseptic*, *i.e.*, it hinders putrefaction, and is applied, either alone or in combination with glycerine, for the preservation of milk, meat, and other foods. It is also said to kill grass.

* According to Hehner, boric acid can be completely volatilised at 100° C. without at any stage having the composition $H_2O.B_2O_3$.

A characteristic property of boric acid is that of imparting a green colour to flames. Its presence may thus be detected in the steam issuing from a boiling solution of boric acid in water; for if a spirit-flame or a piece of burning paper is held in the steam, the flame acquires a green tint, especially at the edges.

The colour is more distinctly seen when the crystallised boric acid is heated on platinum foil in a spirit-flame or an air-gas flame; and still better when the crystals are dissolved in boiling alcohol, and the solution burnt on a plate. The presence of boric acid in borax may be ascertained by mixing the solution of borax with strong sulphuric acid to liberate the boric acid, and adding enough alcohol to make the mixture burn; or by moistening the borax with glycerine, when it gives a green flame in the Bunsen burner. Another peculiar property of boric acid is its action upon turmeric. If a piece of turmeric paper be dipped in solution of boric acid and dried at a gentle heat, it assumes a fine brown-red colour, which is changed to green or blue by potash or its carbonate. In applying this test to borax, the solution is slightly acidified with hydrochloric acid, to set free the boric acid, before dipping the paper. In the presence of oxalic acid the test is more delicate.

Borates.—Boric acid, like carbonic, must be classed among the feeble acids. It colours litmus violet only, like carbonic acid, and does not neutralise the action of the alkalies upon test-papers. At high temperatures, fused boric anhydride combines with the alkalies and metallic oxides to form transparent glassy borates, which have, in many cases, very brilliant colours, and upon this property depend the chief uses of boric acid in the arts.

Unlike the silicates, the borates are comparatively rare in the mineral world. No very familiar mineral substance, except borax, contains boric acid. A double borate of sodium and calcium, called *boro-natrocalcite*, $Na_2B_4O_7.(CaB_4O_7)_2.18H_2O$, is imported from Peru for the manufacture of borax, and the mineral known as *boracite* is a magnesium borate. The mineral *tourmaline*, an aluminium-ferrous silicate, contains a considerable proportion of B_2O_3, apparently substituted for part of the Al_2O_3.

In determining the proportion of base which boric acid requires to form a chemically neutral salt, the same difficulties are met with as in the case of silicic acid (p. 280); but since it is found that 69.8 parts of boric anhydride (the weight represented by B_2O_3) displace 54 parts of water (three molecules) from sodium hydroxide and from barium hydroxide, each employed in excess, it would appear that the boric acid requires three molecules of an alkali fully to satisfy its acid character, $6NaOH + B_2O_3 = 2Na_3BO_3 + 3H_2O$. Hence, boric acid is a tribasic acid represented by the formula H_3BO_3, which is the composition of the crystallised acid, but the formulæ of the common borates cannot be made to accord with this view. The only *orthoborate* yet obtained is $Mg_3(BO_3)_2$.

The acid character of boron oxide (B_2O_3) is so feeble as compared with that of such anhydrides as SO_3 and P_2O_5, that boron oxide can even behave as a feeble base towards these powerful acid oxides, forming salts such as $B_2O_3.P_2O_5$.

By treating borates with H_2O_2, or by electrolysing them as for the production of persulphates (p. 235), perborates such as Na_3BO_4 are obtained. They are unstable and rapidly lose oxygen.

146. **Boron.**—It was in the year 1808 that Gay-Lussac and Thénard succeeded, by fusing boric anhydride with potassium, in isolating boron. The element is more easily prepared by fusing magnesium with an excess of boric acid and treating the product successively with alkalies and acids. The *amorphous boron* thus obtained is a maroon-coloured powder of sp. gr. 2.45. It is infusible, burns with a green flame at 700° C., and is a very poor conductor of electricity. This form of

boron is attacked by hot concentrated mineral acids; it behaves like charcoal in its tendency to absorb gases.

The so-called *diamond of boron* is obtained by very strongly heating amorphous boron with aluminium, extracting the aluminium from the mass with hydrochloric acid, and afterwards separating the crystals of mixed boron and aluminium from those of boron by boiling with nitric acid. These crystals are brilliant transparent octahedra (sp. gr. 2.68), which are sometimes nearly colourless, and resemble the diamond in their power of refracting light, and in their hardness, which is so great that they will scratch rubies, and will even wear away the surface of the diamond.* This form of boron cannot be attacked by any acid, but is dissolved by fused alkalies. It only undergoes superficial conversion into boric anhydride when heated to whiteness in oxygen.

Boron forms a compound with hydrogen which has never been obtained free from admixed hydrogen, but probably has the formula BH_3; it is an inflammable gas, burning with a green flame, and is obtained by heating fused boric anhydride with magnesium and treating the mass with hydrochloric acid. Boron shows greater disposition to combine with nitrogen than is manifested by most other elements. It absorbs nitrogen readily when heated to redness, forming a white infusible insoluble powder, the *boron nitride* (BN).

Boron nitride is also obtained by heating to redness anhydrous borax with twice its weight of ammonium chloride and extracting with dilute HCl which leaves the nitride undissolved. When heated in steam it yields boric acid and ammonia; $BN + 3H_2O = H_3BO_3 + NH_3$. When heated in air it phosphoresces greenish.

Boron carbide, CB_6, is produced when boron and carbon are heated together in the electric furnace, best in the presence of silver which dissolves both elements and enables the carbide to crystallise. It is black and remarkably hard, ranking next to diamond in this respect. It burns in oxygen at a high temperature, and is attacked by fused alkalies but not by acids.

Boron trichloride, BCl_3.—Boron burns when heated at 410° C. in chlorine forming the trichloride, which is more conveniently prepared by heating a mixture of boric acid and charcoal in chlorine; $B_2O_3 + C_3 + Cl_6 = 2BCl_3 + 3CO$. It is a liquid of sp. gr. 1.35 and boils at 17° C. It is the chloranhydride (p. 191) of metaboric acid, being decomposed by water thus: $BCl_3 + 3H_2O = B(OH)_3 + 3HCl$. It has a remarkable tendency to combine with other chlorides.

147. *Boron trifluoride* (BF_3), may be prepared by strongly heating a mixture of powdered boric anhydride with twice its weight of fluor spar in an iron tube; $3CaF_2 + B_2O_3 = 3CaO + 2BF_3$.

The boron fluoride is a gas which fumes strongly in moist air, like the silicon fluoride. It is absorbed eagerly by water, with evolution of heat. One volume of water at 0° C. is capable of dissolving 1057 volumes of boron fluoride, producing a corrosive heavy liquid (sp. gr. 1.77), which fumes in air, and chars organic substances on account of its attraction for water. This solution is known as *fluoboric* or *borofluoric acid*, and its formation is explained by the equation $2BF_3 + 3H_2O = B_2O_3.6HF$ (*Fluoboric acid*).

When the solution is heated, it evolves boron fluoride, until its specific gravity is reduced to 1.58, when it distils unchanged.

Hydrofluoboric acid is obtained in solution by adding a large quantity of water to fluoboric acid; $2(B_2O_3.6HF) = H_3BO_3 + 3H_2O + 3HBF_4$ (*hydrofluoboric acid*).

* The author has known them to cut through the bottom of the beaker used in separating them from the aluminium.

The hydrogen of this acid may be exchanged for metals to form *borofluorides*, which have been applied as antiseptics. Ammonium borofluoride NH_4BF_4 is produced when boron nitride is heated with hydrofluoric acid.

Boron trisulphide, B_2S_3, is made by strongly heating boron in H_2S; it forms white needles, melts at 310° C., and yields $B(OH)_3$ and H_2S when in contact with water. *Boron pentasulphide*, B_2S_5, is a white crystalline powder (m.p. 390° C.) made by heating BI_3 with S in CS_2 at 60°. It is decomposed by water into $B(OH)_3$, H_2S and S.

PHOSPHORUS.

P = 31 parts by weight.*

148. This element is never known to occur uncombined in nature, but is found abundantly in the form of *phosphate of lime* or *tricalcic diphosphate*, $3CaO.P_2O_5$ or $Ca_3(PO_4)_2$, which is contained in the minerals *coprolite*, *phosphorite*, and *apatite*, and occurs diffused, though generally in small proportion, through all soils upon which plants will grow; for phosphorus, probably in this form, is an essential constituent of the food of plants, and especially of the cereal plants, which form so large a proportion of the food of animals. The seeds of such plants are especially rich in the phosphates of calcium and magnesium.

Animals feeding upon these plants still further accumulate the phosphorus, for it enters, chiefly in the form of calcium phosphate, into the composition of almost every solid and liquid in the animal body, and is especially abundant in the bones, which contain about three-fifths of their weight of calcium phosphate.

Composition of the Bones of Oxen.

Fat	5.4
Nitrogenous matter	28.6
Calcium phosphate	56.5
„ fluoride	1.2
„ carbonate	7.3
Magnesium phosphate	1.0
	100.00

What is here termed nitrogenous matter is a cartilaginous substance, converted into gelatine when the bones are heated with water under pressure, and containing C, H, N and O. It was formerly the custom to get rid of this by burning the bones in an open fire, but the increased demand for chemical products, and the diminished supply of bones, have taught economy, so that the cartilaginous matter is now dissolved out by heating the bones with water at a high pressure for the manufacture of glue; or the bones are subjected to destructive distillation, so as to save the ammonia which they evolve, and the bone charcoal thus produced is used by the sugar-refiner until its decolorising powers are exhausted, when it is heated in contact with air to burn away the charcoal, and leave the *bone-ash*, consisting chiefly of calcium phosphate, $Ca_3(PO_4)_2$, and valuable as a manure.

Originally, phosphorus was made from bone-ash, but now the cheaper calcium phosphate of mineral origin is employed as the raw material. The coprolites, or other phosphates, are ground to powder and mixed with enough chamber acid (H_2SO_4) to convert the calcium into sulphate and to liberate the phosphoric acid; $Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4$. The liquor is evaporated and the solution of phosphoric acid

* The vapour of phosphorus is 62 times as heavy as hydrogen, so that its atom only occupies half a volume, if the atom of hydrogen be taken to occupy one volume; and the molecule of phosphorus (P_4) occupying two volumes, would consist of four atoms instead of two. At very high temperatures the specific gravity of phosphorus vapour diminishes, showing a tendency to conform with the ordinary law of volumes.

separated from the calcium sulphate by filtration. This solution is further evaporated to a syrup, absorbed by charcoal and dried, during which the phosphoric acid loses water, becoming metaphosphoric acid, $H_3PO_4 = HPO_3 + 2H_2O$. It is now only necessary to distil the mixture of charcoal and metaphosphoric acid in bottle-shaped fireclay retorts set in a furnace. The phosphorus distils, hydrogen and carbon monoxide being evolved at the same time ($4HPO_3 + C_{12} = 12CO + P_4 + H_4$), and is condensed under warm water in which it melts. It is far from pure, having a mahogany colour; to eliminate this it is remelted with a mixture of sulphuric acid and potassium bichromate; the impurities are thus oxidised and the phosphorus becomes yellow. It is cast into sticks or wedges which are packed in tins, containing water, for the market. The yield is only 70 per cent. of the theoretical yield.

Instead of liberating the phosphoric acid from the calcium phosphate by sulphuric acid as described above, advantage may be taken of the fact that at very high temperatures silicic anhydride (SiO_2), being less volatile than phosphoric anhydride (P_2O_5), can expel the latter from its combination with lime, although a less powerfully acid oxide; $Ca_3(PO_4)_2 + 3SiO_2 = 3CaSiO_3 + P_2O_5$. The temperature of the electric furnace (p. 138), however, is essential for this reaction; accordingly, on a commercial scale a mixture of calcium phosphate, sand (SiO_2) and coke (C) is heated in such a furnace provided with an arrangement for collecting the phosphorus which distils from the mixture. The carbon of the coke reduces the P_2O_5 liberated according to the above equation; $P_2O_5 + C_5 = P_2 + 5CO$.

On a small scale, for the sake of illustration, phosphorus may be prepared by a process which has also been successfully employed for its manufacture in quantity, and consists in heating a mixture of bone-ash and charcoal in a stream of hydrochloric acid gas; $Ca_3(PO_4)_2 + 6HCl + C_6 = 3CaCl_2 + 8CO + H_6 + P_2$.

A mixture of equal weights of well-dried charcoal and bone-ash, both in fine powder, is introduced into a porcelain tube, and placed in a gas furnace. One end of the tube is connected with a flask evolving HCl (p. 177), and the other is cemented with putty into a bent tube for conveying the phosphorus into a vessel of water. On heating the porcelain tube to bright redness, phosphorus distils in abundance. The hydrogen and carbonic oxide inflame as they escape into the air, from their containing phosphorus vapour.

Pure ordinary, or *vitreous*, phosphorus is almost colourless and transparent, but when exposed to light, and especially to direct sunlight, it gradually acquires an opaque red colour, from its conversion into the allotropic variety known as *red phosphorus*. By tying bands of black cloth round a stick of phosphorus and exposing it, under water, to the action of sunlight, alternate zones of red may be produced.

Even though the phosphorus be screened from light, it will not remain unchanged unless the water be kept quite free from air, which irregularly corrodes the surface of the phosphorus, rendering it white and opaque. This action is accelerated by exposure to light.

The most remarkable character of ordinary phosphorus is its easy inflammability. It inevitably takes fire in air when heated a little above its melting-point, 44° C. (111°.5 F.), burning with a brilliant white flame, which becomes insupportable when the combustion is in oxygen (p. 34), and evolving dense white clouds of phosphoric anhydride. When a piece of dry phosphorus is exposed to the air, it combines

slowly with oxygen,* and its temperature often becomes so much elevated during this slow combustion, that it melts and takes fire, especially if the combustion be encouraged by the warmth of the hand or by friction. Hence, ordinary phosphorus must never be handled or cut in the dry state, but always under water, for it causes most painful burns.

The slow oxidation of phosphorus is attended with that peculiar luminous appearance which is termed *phosphorescence* (*φῶς, light, φέρω, to bear*), but this glow is not seen in pure oxygen, except under diminished pressure, or in air containing a minute proportion of olefiant gas or oil of turpentine; nor will phosphorus glow in compressed air at the ordinary temperature. It will be remembered that the slow oxidation of phosphorus in moist air is attended with the formation of ozone.

The glow of phosphorus, which may be regarded as an incipient flame, is in some way connected with this ozone (possibly produced during the oxidation of the phosphorus to P_2O_5; $P_2 + 3O_2 = P_2O_5 + O$ and $O_2 + O = O_3$). When phosphorus is exposed to pure oxygen at the ordinary pressure, oxidation seems to proceed very slowly at the ordinary temperature; but at an elevated temperature (25° C), or in oxygen at diminished pressure,† the phosphorus is oxidised with formation of P_2O_5 (and ozone) and P_4O_6. This latter oxide is readily oxidised to P_2O_5 and phosphoresces during the change, particularly in the presence of ozone. Moisture is essential to the oxidation (and the glow) of phosphorus at any pressure.

Ordinary phosphorus is slowly vapourised at common temperatures, and emits in the air white fumes with a peculiar alliaceous odour, which appear phosphorescent in the dark. It boils at 278° C., yielding a colourless vapour.

The characteristic behaviour of phosphorus in air is best observed when the phosphorus is in a finely divided state. The experiment described on p. 34 (Fig. 26) will serve as an illustration.

If phosphorus be dissolved in olive oil, at a gently heat, the solution is strongly phosphorescent when shaken in a bottle containing air, or rubbed upon the hand.

Characters may be written on paper with a stick of phosphorus held in a thickly folded piece of damp paper (having a vessel of water at hand into which to plunge the phosphorus if it should take fire). When the paper is held with its back to the fire, or to a hot iron, in a darkened room, a twinkling combustion of the finely divided phosphorus ensues and the letters are burnt into the paper. Phosphorus which has been partly oxidised is even more easily inflamed than pure phosphorus. If a few small pieces of phosphorus be placed in a dry stoppered bottle, gently warmed till they melt, and then shaken round the sides of the bottle so as to become partly converted into red oxide of phosphorus, it will be found, long after the bottle is cold, to be spontaneously inflammable, so that if a wooden match tipped with sulphur be rubbed against it, the phosphorus which it takes up will ignite when the match is brought into the air, kindling the sulphur, which will inflame the wood. This was one of the earliest forms in which phosphorus was employed for the purpose of procuring an instantaneous light. If the stopper be greased, the phosphorus may be preserved unchanged for a long time.

In the last experiment, if the wood had not been tipped with sulphur, the

* The white fumes evolved by phosphorus in moist air are said to consist partly of ammonium nitrate, formed by the action of the ozonised oxygen (p. 65) upon the air and aqueous vapour.

† It will be remembered that the pressure of the oxygen in the air is only about one-fifth of the total pressure, so that air contains oxygen at diminished pressure. The extent to which the pressure must be diminished for the production of the glow depends on the temperature.

phosphorus would not have kindled it, the flame of phosphorus generally being unable to ignite solid combustibles, because it deposits upon them a coating of P_2O_5, which protects them from the action of air. Hence, in the manufacture of lucifer matches, the wood is first tipped with sulphur, or wax, or paraffin, which easily give off combustible vapours to be kindled by the flame of the phosphorus composition, and thus to inflame the wood.

If a small stick of phosphorus be carefully dried with filtering paper, and dropped into a cylinder of oxygen, which is afterwards covered with a glass plate, no luminosity will be observed in a darkened room until the cylinder is placed under the air-pump receiver, and the air slowly exhausted. When the oxygen has thus been rarefied to about one-fifth of its former density, the phosphorescence will be seen. A similar effect may be produced by covering the cylinder of oxygen containing the phosphorus (having removed the glass plate) with another cylinder, about four times its size (Fig. 184), filled with carbonic acid gas, which will gradually dilute the oxygen and produce the phosphorescence. By suspending—in a bottle of air containing a strongly luminous piece of phosphorus—a piece of paper with a drop of oil of turpentine upon it, the glow may be almost instantaneously destroyed. A small tube of olefiant gas or coal gas dropped into the bottle will also extinguish the luminosity.*

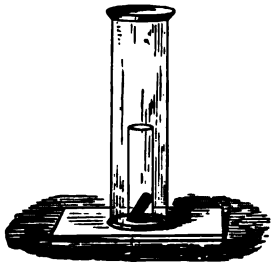


Fig. 184.

The luminosity of phosphorus vapour is seen to advantage when a piece of phosphorus is boiled with water in a narrow-necked flask or retort, or a test-tube with a cork and narrow tube. The steam charged with vapour of phosphorus has all the appearance of a blue flame, in a darkened room, but of course combustibles are not inflamed by it, since its temperature is not higher than 100° C. Phosphorus may be distilled, with perfect safety, in an atmosphere of carbonic acid gas, the neck of the retort being allowed to dip under water in the receiver.

Advantage is taken of the fact that phosphorus distils in steam and renders it luminous in testing for this poison in organic liquids. Very small quantities may thus be detected. Conversely, the glow of phosphorus vapour may serve as a delicate test for oxygen, as it can be detected until the last trace of this gas has disappeared.

Although ordinary phosphorus is of a decidedly glassy or *vitreous* structure, it may be obtained in dodecahedral crystals, by allowing its solution in carbon disulphide to evaporate in an atmosphere of carbonic acid gas, or by fusing it in a tube exhausted by a Sprengel pump, and letting it cool in the dark.

The conversion of ordinary phosphorus into the *red phosphorus* is one of the most striking instances of allotropic modification. When phosphorus is heated for a considerable length of time to about 450° F. (232° C.) *in vacuo*, or in an atmosphere in which it cannot burn, it becomes converted into an infusible mass of red phosphorus, 27,000 gram units of heat being evolved for every 31 grams converted. This form of phosphorus differs as widely from the vitreous form as graphite differs from diamond. It is only slowly oxidised in warm moist air, evolves no vapour, is not luminous, cannot be inflamed by friction, or even by any heat short of 500° F. (260° C.) When it is heated above 350° C. it slowly sublimes as yellow phosphorus. By heating vitreous phosphorus in an exhausted and sealed tube to about 500° C., it is converted into a violet-black fused mass with cavities containing crystals. Red phosphorus is insoluble in the solvents for ordinary phosphorus. The two varieties also differ greatly in specific gravity, that of the

* Chappuis finds that when phosphorus is suspended in oxygen, the space glows for a short time on adding a little ozone.

ordinary phosphorus being 1.83, and of the red variety 2.14. Of the two, the red variety is the better conductor of electricity.

The conversion of vitreous into red phosphorus, or *amorphous phosphorus* as it was called before it was proved to be microscopically crystalline, may be effected by heating it in a flask (A, Fig. 185) placed in an oil-bath (B), maintained at a temperature ranging from 450° to 460° F. (232° to 238° C.), the flask being furnished with a bent tube (C) dipping into mercury, and with another tube (D) for supplying carbonic acid gas, dried by passing over calcium chloride. The flask should be thoroughly filled with carbonic acid gas before applying heat, and the tube delivering it may then be closed with a small clamp (E). After exposure to heat for about forty hours, but little ordinary phosphorus will remain, and this may be removed by allowing the mass to remain in contact with carbon disulphide for some hours, and subsequently washing it with fresh disulphide till the latter leaves no phosphorus when evaporated.

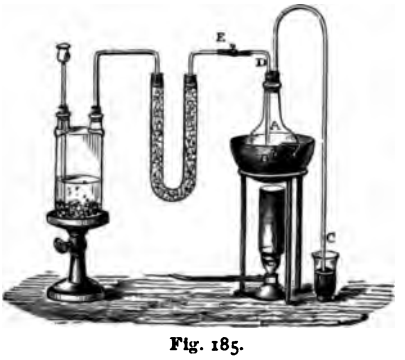


Fig. 185.

On the large scale, the red phosphorus is prepared by heating about 200 lbs of vitreous phosphorus to 450° F. (232° C.) in an iron boiler. After three or four weeks the phosphorus is found to be converted into a hard red brittle mass, which is ground by millstones under water, and separated from the ordinary phosphorus either by carbon disulphide or caustic soda, in which the latter is soluble. The temperature requires careful regulation, for if it be allowed to rise to 350° C., the red phosphorus resumes the vitreous condition. This reconversion may be shown by heating a little red phosphorus in a narrow test-tube, when drops of vitreous phosphorus condense on the cool part of the tube. The colour of different specimens of red phosphorus varies considerably, depending upon the temperature at which the conversion has been effected ; that prepared on the large scale is usually of a dark purplish colour, but it may be obtained of a bright scarlet colour. Rhombohedral crystals of the red phosphorus, resembling crystals of arsenic in form and metallic appearance, have been obtained by fusing phosphorus with lead, and dissolving out the latter with diluted nitric acid (sp. gr. 1.1). Similar crystals have been obtained by heating red phosphorus to 530° C. in a vacuous tube.

Ordinary phosphorus is very poisonous (0.1 gram being fatal), whilst red phosphorus appears to be harmless. The former is employed, mixed with fatty substances, for poisoning rats and beetles. Cases are, unhappily, not very rare, of children being poisoned by sucking the phosphorus composition on lucifer matches. The vapour of phosphorus also produces a very injurious effect upon the persons engaged in the manufacture of lucifer matches, resulting in the decay of the lower jaw-bone. The evil is much mitigated by good ventilation, or by diffusing turpentine vapour through the air of the workroom, and attempts have been made to obviate it entirely by substituting red phosphorus for the ordinary variety, but, as might be expected, the matches thus made are not so sensitive to friction as those in which the vitreous phosphorus is used.

The difference between the two varieties of phosphorus, in respect to chemical energy, is seen when they are placed in contact with a little iodine on a plate, when the ordinary phosphorus undergoes combustion and the red phosphorus remains unaltered.

Ordinary phosphorus, when moist, is capable of direct union with

oxygen, chlorine, bromine, iodine, sulphur, and most of the metals, with which it forms *phosphides* or *phosphurets*. Even gold and platinum unite with this element when heated, so that crucibles of these metals are liable to corrosion when heated in contact with a phosphate in the presence of a reducing agent, such as carbon. Thus the inside of a platinum dish or crucible is roughened when vegetable or animal substances containing phosphates are incinerated in it. The presence of small quantities of phosphorus in iron or copper produces considerable effect upon the physical qualities of these metals.

Phosphorus has the property, a very remarkable one in a non-metal, of precipitating some metals from their solutions in the metallic state. If a stick of phosphorus be placed in a solution of sulphate of copper, it becomes coated with metallic copper, the phosphorus appropriating the oxygen. This has been turned to advantage in copying very delicate objects by the electrotype process, for by exposing them to the action of a solution of phosphorus in ether or carbon disulphide, and afterwards to that of a solution of copper, they acquire the requisite conducting metallic film, even on their finest filaments. Solutions of silver and gold are reduced in a similar manner by phosphorus.

By floating very minute scales of ordinary phosphorus upon a dilute solution of chloride of gold, the metal will be reduced in the form of an extremely thin film, which may be raised upon a glass plate, and will be found to have various shades of green and violet by transmitted light, dependent upon its thickness, whilst its thickest part exhibits the ordinary colour of the metal to reflected light. By heating the films on the plate, various shades of amethyst and ruby are developed. If a very dilute solution of chloride of gold in distilled water be placed in a perfectly clean bottle, and a few drops of ether, in which phosphorus has been dissolved, poured into it, a beautiful ruby-coloured liquid is obtained, the colour of which is due to metallic gold in an extremely finely divided state, and on allowing it to stand for some months, the metal subsides as a purple powder, leaving the liquid colourless. If any saline impurity be present in the gold solution, the colour of the reduced gold will be amethyst or blue. These experiments illustrate very strikingly the use of gold for imparting ruby and purple tints to glass and the glaze of porcelain.

149. *Lucifer matches* are made by tipping the wood with sulphur, or wax, or paraffin, to convey the flame, and afterwards with the match composition, which is generally composed of saltpetre or potassium chlorate, phosphorus, red lead, and glue, and depends for its action on the easy inflammation, by friction, of phosphorus when mixed with oxidising agents like saltpetre (KNO_3), potassium chlorate ($KClO_3$), or red lead (Pb_3O_4), the glue only serving to bind the composition together and attach it to the wood. The composition used by different makers varies much in the nature and proportions of the ingredients. In this country, potassium chlorate is most commonly employed as the oxidising agent, such matches usually kindling with a slight detonation; but the German manufacturers prefer either potassium nitrate or lead nitrate, together with lead dioxide or red lead, which produce *silent matches*.

Sulphide of antimony (which is inflamed by friction with potassium chlorate, see p. 186) is also used in those compositions in which a part of the phosphorus is employed in the red form, and fine sand or powdered glass is very commonly added to increase the susceptibility of the mixture to inflammation by friction.

The match composition is coloured either with ultramarine blue, Prus-

sian blue, or vermilion. In preparing the composition, the glue and the nitre or chlorate are dissolved in hot water, the phosphorus then added and carefully stirred in until intimately mixed, the whole being kept at a temperature of about 100° F. (38° C.). The fine sand and colouring matter are then added, and when the mixture is complete, it is spread out upon a stone slab heated by steam, and the sulphured ends of the matches are dipped into it.

The *safety matches*, which refuse to ignite unless rubbed upon the sides of the box, are tipped with a mixture of antimony sulphide, potassium chlorate and powdered glass, which is not sufficiently sensitive to be ignited by any ordinary friction, but inflames at once when rubbed upon the red phosphorus mixed with glass, which coats the rubber on the sides of the box.

It would be very desirable to dispense entirely with the use of phosphorus in lucifer matches, not only because of the danger from accident and disease in the manufacture, but because a certain quantity of phosphate of lime is diverted from agricultural purposes to the preparation of phosphorus, of which many tons are consumed annually for the manufacture of matches. The most successful attempt in this direction appears to be the employment of a mixture of potassium chlorate and lead hyposulphite, in place of the ordinary phosphorus composition.

For illustration, very excellent matches may be made upon the small scale in the following manner. The slips of wood are dippped in melted sulphur so as to acquire a slight coating. Thirty grains of gelatine or isinglass are dissolved in 2 drachms of water in a porcelain dish placed upon a steam-bath ; 20 grains of ordinary phosphorus are then added, and well mixed in with a piece of wood ; to this mixture are added, in succession, 15 grains of red lead and 50 grains of powdered potassium chlorate. The sulphured matches are dipped into this paste, and left to dry in the air.

To make the safety matches : 10 grains of powdered potassium chlorate and 10 grains of antimony sulphide are made into a paste with a few drops of a warm solution of 20 grains of gelatin in 2 drachms of water, the sulphured matches being tipped with this composition. The rubber is prepared with 20 grains of red phosphorus, and 10 grains of finely-powdered glass, mixed with the solution of gelatine, and painted on paper or cardboard with a brush.

150. A very sensitive detonating composition formerly used for igniting percussion shells, may be prepared *with care* in the following manner : Four grains of powdered potassium chlorate are moistened on a plate with 6 drops of spirit of wine, 4 grains of powdered red phosphorus are added, and the whole mixed, at arm's length, with a bone-knife, avoiding great pressure. The mixture, which should be quite moist, is spread in small portions upon ten or twelve pieces of filtering paper, and left in a safe place to dry. If one of these be gently pressed with a stick, it explodes with great violence. It is dangerous to press it with the blade of a knife, as the latter is commonly broken, and the pieces projected with considerable force. A stick dipped in oil of vitriol of course explodes it immediately. If a bullet be placed very lightly upon one of the pellets, and the paper tenderly wrapped round it, a percussion shell may be extemporised, which explodes with a loud report when dropped upon the floor.

The detonating toys known as *amorces fulminantes* are made by enclosing this composition between two pieces of thin paper. 1000 of them contain 70 grains of the composition.

151. **Oxides of Phosphorus.**—Four compounds of phosphorus and oxygen are known, their formulæ being P_4O, P_4O_6, P_2O_4, and P_2O_5. Of these P_4O_6 and P_2O_5 are anhydrides, the others are neutral oxides.

Phosphoric Acids and Phosphates.

152. The phosphates are by far the most important of the compounds of phosphorus. They have been already noticed as almost the only forms of combination in which that element is met with in nature, and as indispensable ingredients in the food of plants and animals. No other mineral substance can bear comparison with calcium phosphate as a measure of the capability of a country to support animal life. Phosphoric acid itself is very useful in calico-printing and in some other arts.

The mineral sources of this acid appear to be *phosphorite*, *coprolite*, and *apatite*, all consisting essentially of calcium phosphate, $Ca_3(PO_4)_2$, but associated in each case with calcium fluoride, which is also contained, with calcium phosphate, in bones, and would appear to indicate an organic origin for these minerals. Phosphorite is any earthy-looking substance, forming large deposits in Estremadura. Apatite (from *ἀπατάω*, *to cheat*, in allusion to mistakes in its early analysis) occurs in prismatic crystals, and is met with in the Cornish tin-veins. Both these minerals are largely imported from Spain, Norway, and Florida, for use in this country as a manure. Coprolites (*κόπρος*, *dung*, *λίθος*, *a stone*, from the idea that they were petrified dung) are rounded nodules of calcium phosphate, which are found abundantly in this country.

Large quantities of phosphates of calcium and magnesium are imported in the form of *guano*, the partially decomposed excrement of sea fowl.

Phosphoric acid is obtained from bone-ash, or mineral phosphate, by decomposing it with sulphuric acid, so as to remove as much of the lime as possible in the form of sulphate, which is strained off, and the acid liquid neutralised with ammonium carbonate, which precipitates any unchanged calcium phosphate, and converts the phosphoric acid into ammonium phosphate. On evaporating the solution, and heating the ammonium phosphate, ammonia and water are expelled, and metaphosphoric acid (HPO_3) is left in a fused state, solidifying to a glass on cooling. Thus prepared, however, it always retains some ammonia.

This method of preparing phosphoric acid is illustrative of one very generally employed in the preparation of those acids which cannot be distilled. In the case of most of the acids heretofore considered, advantage is taken of their great volatility, compared with that of sulphuric acid, to obtain them from their sodium salts. It is possible to liberate phosphoric acid from its sodium salt by the action of sulphuric acid; but since phosphoric acid is not more volatile than sulphuric acid, it is difficult to separate the sodium sulphate produced by the combination of the sulphuric acid with the sodium of the sodium phosphate, from the phosphoric acid, both of them remaining in solution. In such cases advantage is taken of the insolubility of calcium sulphate or of barium sulphate; when a calcium or barium salt of the required acid is treated with sulphuric acid, calcium sulphate or barium sulphate is precipitated, and may be separated from the solution containing the desired acid by filtration. The treatment of a lead salt of the acid with hydrosulphuric acid, whereby lead sulphide is precipitated, is another method for preparing acids, based on the same principle.

Pure phosphoric acid is prepared by oxidising phosphorus with dilute

nitric acid (sp. gr. 1.197) and evaporating the solution until the phosphoric acid begins to volatilise in white fumes; $5HNO_3 + P_2 = 3HPO_3 + H_2O + 5NO$.* Some phosphorous acid is formed at an intermediate stage. A transparent glass (*glacial phosphoric acid*) is thus obtained, which eagerly absorbs moisture from the air, and becomes liquid. That which is sold in sticks contains much sodium metaphosphate.

The addition of a little bromine greatly facilitates the action of nitric acid upon phosphorus, apparently by forming the phosphorus pentabromide, which is then decomposed by water; $PBr_5 + 4H_2O = H_3PO_4 + 5HBr$. The hydrobromic acid being then acted on by nitric acid, bromine is set free to act upon a fresh quantity of phosphorus; $3HBr + HNO_3 = Br_2 + 2H_2O + NO$. When iodine is also added, the action is still better. 28 grams of phosphorus are placed in 170 c.c. of water and 0.32 gram of iodine are added; then, drop by drop, 1.94 grams of bromine. When the action is over, 170 c.c. of HNO_3 (sp. gr. 1.42) are added, and the vessel is placed in cold water. When the phosphorus has dissolved, the solution is evaporated till its temperature rises to about 204° C. in order to expel the excess of nitric acid, the bromine, and the iodine.

Phosphoric anhydride, or **phosphorus pentoxide** (P_2O_5), is prepared by burning phosphorus in dry air.

When required in considerable quantity, the anhydride is prepared by burning the phosphorus in a small porcelain dish (A, Fig. 186) placed under a bell-jar which fits in a groove containing mercury and surrounding a glass funnel. Air

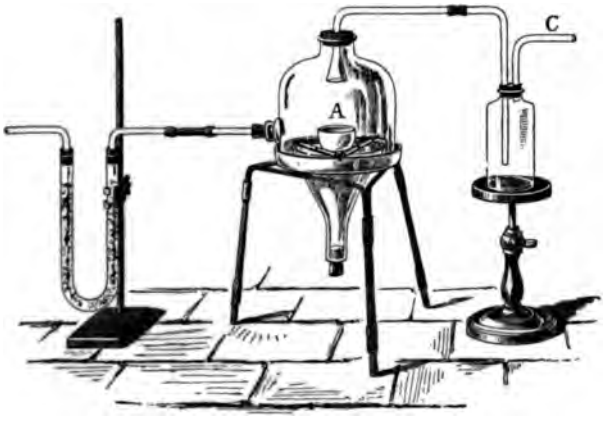


Fig. 186.

is drawn through the apparatus by an aspirator attached to the tube C, the empty bottle serving to catch the P_2O_5 carried over by the current. A drying-tube, containing pumice moistened with oil of vitriol, is attached to the lateral neck of the bell-jar in order to dry the entering air. When all the phosphorus has been burnt the bell may be removed, and the P_2O_5 swept down the stem of the funnel into a dry bottle. A small quantity of phosphoric anhydride is more conveniently prepared by burning phosphorus under a large bell-jar, as shown in Fig. 25.

Phosphoric anhydride as thus prepared is amorphous; it may be fused at a very high temperature, and even sublimed, when it condenses as microscopic crystals. Its great feature is its attraction for water; left exposed to the air for a very short time it deliquesces entirely, becoming converted into phosphoric acid. It is often used by chemists as a

* Orthophosphoric acid is first formed, $5NO_2OH + P_2 + 2HOH = 3PO(OH)_3 + 5NO$; but this loses water during the evaporation, $PO(OH)_3 - H_2O = PO_2(OH)$.

de-hydrating agent, and will even remove water from oil of vitriol. When thrown into water it hisses like a red-hot iron, but does not entirely dissolve at once, a few flakes of metaphosphoric acid (?) remaining suspended in the liquid for some time. The commercial anhydride is apt to contain lower oxides of phosphorus, and even red phosphorus.

The solution obtained by dissolving phosphoric anhydride in water contains *monohydrated phosphoric acid* or *metaphosphoric acid* ($H_2O.P_2O_5$ or HPO_3) the analogue of nitric acid. If a little silver nitrate be added to a portion of it, a transparent gelatinous precipitate is formed, which is the silver metaphosphate ($AgNO_3 + HPO_3 = HNO_3 + AgPO_3$).

If the solution of metaphosphoric acid is heated in a flask for a short time, it loses the property of yielding a precipitate with silver nitrate, unless one or two drops of ammonia be added to neutralise it, when an opaque white precipitate of silver pyrophosphate ($2Ag_2O.P_2O_5$ or $Ag_4P_2O_7$) is obtained, for the phosphoric acid has now been converted into the *dihydrated* or *pyrophosphoric acid* ($2H_2O.P_2O_5$ or $H_4P_2O_7$). The formation of the precipitate is thus expressed—

$$H_4P_2O_7 + 4AgNO_3 + 4NH_3 = Ag_4P_2O_7 + 4NH_4NO_3.$$

When the solution of pyrophosphoric acid is mixed with more water and boiled for a long time, it gives, when tested with silver nitrate and a little ammonia, a yellow precipitate of silver orthophosphate, ($3Ag_2O.P_2O_5$ or Ag_3PO_4); the phosphoric acid having become converted into *trihydrated phosphoric acid* or *orthophosphoric acid* ($3H_2O.P_2O_5$ or H_3PO_4), and acting upon the silver nitrate in the presence of ammonia, thus $H_3PO_4 + 3AgNO_3 + 3NH_3 = Ag_3PO_4 + 3NH_4NO_3$.

The reverse changes occur when orthophosphoric acid is heated, this becoming pyrophosphoric acid at 300° C., and metaphosphoric acid at a red heat.

The *pyrophosphoric acid* ($H_4P_2O_7$) cannot be obtained by the above process without an admixture of one of the other acids, but it has been obtained in crystals by decomposing the lead pyrophosphate ($Pb_2P_2O_7$) with hydrosulphuric acid, and evaporating the filtered solution *in vacuo* over oil of vitriol.

Trihydrated phosphoric acid may also be obtained in prismatic crystals, by evaporating its solution in a similar way. This acid is also called *orthophosphoric acid* (ὀρθός, *true*), and *common* phosphoric acid, in allusion to the circumstance that the phosphates found in nature and commonly met with and employed in the arts are the salts of this acid.

Metaphosphoric acid is distinguished from the other two acids by the fact that it coagulates white of egg (albumin).

It will be perceived, from their formulæ, that metaphosphoric, HPO_3, orthophosphoric, H_3PO_4, and pyrophosphoric acid, $H_4P_2O_7$, are respectively monobasic, tribasic, and tetrabasic acids. The normal sodium salts of these acids are, respectively, metaphosphate, $NaPO_3$, orthophosphate, Na_3PO_4, and pyrophosphate, $Na_4P_2O_7$. The hydrogen in orthophosphoric and pyrophosphoric acids may be only partly exchanged for a metal; thus there are two other orthophosphates of sodium, viz., hydrogen-disodium phosphate, HNa_2PO_4, and dihydrogen-sodium phosphate, H_2NaPO_4.

The phosphates commonly met with are all derived from orthophosphoric acid: for example, bone-ash, or tricalcium orthophosphate, $Ca_3(PO_4)_2$; superphosphate, or monocalcium orthophosphate, $CaH_4(PO_4)_2$; common phosphate of soda, or hydrogen-disodium orthophosphate, HNa_2PO_4; microcosmic salt, or hydrogen-ammonium sodium orthophosphate, $HNH_4Na(PO_4)$.

Pyrophosphates and metaphosphates may be obtained by the action of heat on

the orthohydrogen phosphates. Thus, if a crystal of the common rhombic sodium phosphate ($HNa_2PO_4.12Aq$) be heated gently in a crucible, it melts in its water of crystallisation, and gradually dries up to a white mass, the composition of which, if not heated beyond 149° C., will be Na_2HPO_4. A little of this white mass dissolved in water gives a solution *alkaline* to red litmus-paper ; and if silver nitrate (itself *neutral* to test-papers) is added to it, a *yellow* precipitate of silver orthophosphate is obtained, and the solution becomes strongly *acid*—

$$Na_2HPO_4 + 3AgNO_3 = Ag_3PO_4 + 2NaNO_3 + HNO .$$

If the dried sodium phosphate be now strongly heated over a lamp, it will lose water, and become pyrophosphate (πῦρ, *fire*) ; $2Na_2HPO_4 = H_2O + Na_4P_2O_7$. On dissolving this in water, the solution will be *alkaline*, and will give with silver nitrate a *white* precipitate and a *neutral* solution ; $Na_4P_2O_7 + 4AgNO_3 = Ag_4P_2O_7 + 4NaNO_3$.

Microcosmic salt ($NaNH_4HPO_4.4Aq$), when dissolved in water, yields an *alkaline* solution which gives a *yellow* precipitate with silver nitate, the liquid becoming *acid* ; $NaNH_4HPO_4 + 3AgNO_3 = Ag_3PO_4 + NaNO_3 + NH_4NO_3 + HNO_3$.

But if the salt be heated in a crucible, it fuses, evolving water and ammonia, and leaving a transparent glass of sodium metaphosphate ; $NaNH_4HPO_4 = H_2O + NH_3 + NaPO_3$, which may be dissolved by soaking in water, yielding a slightly *acid* solution, which gives a *white* gelatinous precipitate with silver nitrate, the liquid being *neutral* ; $NaPO_3 + AgNO_3 = AgPO_3 + NaNO_3$.

All the phosphates may be converted into orthophosphates, by fusing them with an alkali, or by boiling them for some time with a dilute acid.*

153. **Phosphorus anhydride** (P_4O_6) is a product of the slow combustion of phosphorus, and, by carefully regulating the combustion, may be made to constitute 50 per cent. of the oxides produced, the remainder being P_2O_5. It is prepared by drawing a slow current of air over ignited phosphorus and causing the product to pass, first through a tube maintained at about 60° C., a temperature at which P_2O_5 condenses, and then through a U-tube surrounded by a freezing-mixture wherein the P_4O_6 solidifies. It forms feathery crystals which melt at 22.5° C. ; it boils at 173° C., and is decomposed at higher temperatures (in a sealed tube) according to the equation $2P_4O_6 = 3P_2O_4 + P_2$. It dissolves slowly in cold water, forming phosphorous acid, $P_4O_6 + 6HOH = 4P(OH)_3$; hot water decomposes it with great violence. It burns in oxygen, forming P_2O_5, and in chlorine, forming $POCl_3$ and PO_2Cl (?). Its combustion in oxygen is attended by all the phenomena of phosphorescence shown by phosphorus, but no ozone is produced.

Phosphorus tetroxide, P_2O_4, corresponding with N_2O_4, is obtained as a very deliquescent crystalline sublimate by heating P_4O_6 to about 440° C. in a sealed tube filled with CO_2 ; the white P_4O_6 becomes orange, from the production of red phosphorus, and P_2O_4 sublimes in deliquescent colourless crystals. When dissolved in water it is converted into a mixture of phosphorous and orthophosphoric acids, just as nitric peroxide, N_2O_4, is converted into nitrous and nitric acids ; $P_2O_4 + 3H_2O = H_3PO_4 + H_3PO_3$.

Phosphorous acid, H_3PO_3 or $P(OH)_3$, or $PHO(OH)_2$, is obtained in solution, mixed with phosphoric acid, when sticks of phosphorus arranged in separate tubes open at both ends and placed in a funnel over a bottle, are exposed under a bell-jar, open at the top, to air saturated with aqueous vapour. To obtain the pure acid, chlorine is very slowly passed through phosphorus fused under water, when the phosphorous chloride first formed is decomposed by the water into phosphorous and hydrochloric acids ; $PCl_3 + 3H_2O = P(OH)_3 + 3HCl$. The hydrochloric acid is expelled by a moderate heat, when the phosphorous acid is deposited in prismatic crystals. When heated, it is decomposed into phosphoric acid and gaseous phosphoretted hydrogen ; $4H_3PO_3 = 3H_3PO_4 + PH_3$.

Solution of phosphorous acid gradually absorbs oxygen from the air, becoming phosphoric acid. This tendency to absorb oxygen causes it to act as a reducing-agent upon many solutions ; thus it precipitates finely divided metallic silver from a solution of the nitrate, by which its presence may be recognised in the water in which ordinary phosphorus has been kept. The solution of phosphorous acid even reduces sulphurous acid, producing sulphuretted hydrogen and sulphur, the latter being formed by the action of the sulphuretted hydrogen upon the sulphurous acid ; $H_2SO_3 + 3H_3PO_3 = 3H_3PO_4 + H_2S$. Some metals dissolve in it, evolving PH_3.

* It has been remarked that the *pliancy* of the acid character of phosphoric acid particularly fits it to take part in the vital phenomena. It may be regarded as three acids in one.

If solution of phosphorous acid be poured into a hydrogen apparatus, some PH_3 is formed which imparts a fine green tint to the hydrogen flame.

It is doubtful whether phosphorous acid is dibasic or tribasic, that is, whether it contains 2 or 3 hydroxyl groups. In the former case its formula should be $PHO(OH)_2$ in the latter, $P(OH)_3$.

As the salt Na_3PO_3 has been prepared, the formula $P(OH)_3$ is indicated ; it is supported by the reaction between PCl_3 and HOH.

154. **Hypophosphorous acid**, H_3PO_2 or $PH_2O(OH)$.—When phosphorus is boiled with barium hydroxide and water, the latter is decomposed, its hydrogen combining with part of the phosphorus to form hydrogen phosphide (spontaneously inflammable), which escapes, whilst the oxygen of the water unites with another part of the phosphorus, forming hypophosphorous acid, which acts on the baryta to form barium hypophosphite ; this may be obtained, by evaporating the solution in crystals having the composition $(PH_2O.O)_2Ba$. The action of phosphorus upon barium hydroxide may be represented by the equation—

$$\underset{\text{Barium hydroxide.}}{3Ba(OH)_2} + 6H_2O + P_8 = \underset{\text{Barium hypophosphite.}}{3(PH_2O.O)_2Ba} + 2PH_3.$$

Some barium orthophosphate is also formed at the same time, as the result of a secondary action.

By dissolving the barium hypophosphite in water, and decomposing it with the requisite quantity of sulphuric acid, so as to precipitate the barium as sulphate, a solution is obtained which may be concentrated by careful evaporation. If this hypophosphorous acid be heated, it evolves hydrogen phosphide, and becomes converted into phosphoric acid ; $2H_3PO_2 = H_3PO_4 + PH_3$. When exposed to the air it absorbs oxygen, and becomes converted into phosphorous and phosphoric acids. It is a more powerful reducing-agent than phosphorous acid. The latter acid does not reduce a solution of cupric sulphate, but hypophosphorous acid, when gently warmed with it, gives a brown precipitate of *cuprous hydride* (CuH), which is decomposed by boiling, evolving H and leaving Cu.

When heated, the hypophosphites evolve hydrogen phosphide, and are converted into phosphates. The sodium hypophosphite, $PH_2O.ONa$, is sometimes used in medicine ; its solution has been known to explode with great violence during evaporation, probably from a sudden disengagement of hydrogen phosphide. Hypophosphites, when boiled with caustic alkalies, are converted into phosphates, hydrogen being evolved ; phosphites are unchanged.

Hypophosphoric acid, $H_4P_2O_6$ or $PO(OH)_2.PO(OH)_2$, exists in the water in which phosphorus has been kept.

The following is a summary of the *acids formed by phosphorus with oxygen and hydrogen :*

Hypophosphorous acid	$PH_2O(OH)$
Hypophosphoric acid	$P_2O_2(OH)_4$
Phosphorous ,, ...	$P(OH)_3$
Metaphosphoric ,, ...	$PO_2.(OH)$
Orthophosphoric ,, ...	$PO(OH)_3$
Pyrophosphoric ,, ...	$P_2O_3(OH)_4$

155. *Suboxide of phosphorus*, P_4O, is supposed to constitute the yellow or red residue which is left in the dish when phosphorus burns in air, but it is always mixed with much phosphoric anhydride. It is also said to be obtained by allowing phosphorus to dissolve slowly in an alcoholic solution of NaOH, and then adding an acid, whereupon an orange red powder is precipitated.

Structure of acids.—Attention has already been called to the theory that oxy-acids contain hydroxyl groups and that they owe their basicity to the number of these groups (pp. 104, 191). Since the group OH is monovalent it is reasonable to suppose that the atom of an element would be capable of combining with one of these groups for each atom fixing-power which the element possesses. Thus, the maximum valency of phosphorus being five (as seen from the chloride PCl_5) the acid $P(OH)_5$ might be expected to exist, although it is not known. It is customary to term such hydroxyl compounds of the elements *ortho-acids*, and to regard

other oxy-acids as being derived from the ortho-acids by loss of water; these other oxy-acids are called *anhydro-acids* to express this view.

According to this conception, the name orthophosphoric acid, which has been given to H_3PO_4, is a misnomer, for this acid is really the first anhydro-acid of true orthophosphoric, $P(OH)_5$, which is unknown. Pyro-phosphoric acid is the second and metaphosphoric acid the third anhydro-acid from true orthophosphoric acid, as will be apparent from the following:—

$$P(OH)_5 - H_2O = PO(OH)_3, \text{ "orthophosphoric acid";}$$

$$\left.\begin{matrix}PO(OH)_3\\PO(OH)_3\end{matrix}\right\} - H_2O = \begin{matrix}P\\P\end{matrix}\!\!\begin{matrix}\diagup O(OH)_2\\O\\\diagdown O(OH)_2\end{matrix}, \text{ pyrophosphoric acid;}$$

$$PO(OH)_3 - H_2O = PO_2(OH), \text{ metaphosphoric acid.}$$

Only a few ortho-acids are known, although the existence of several others is indicated by the fact that some of their salts (chiefly organic salts) have been isolated. The ortho-acids are generally very unstable, tending to lose water and to become anhydro-acids. Thus, *orthocarbonic acid*, $C(OH)_4$, has never been prepared, although several organic ortho-carbonates of the type $C(OM)_4$, in which M is an organic basic radicle, are known. It will be remembered that the anhydro-acid, $CO(OH)_2(=C(OH)_4-H_2O)$, carbonic acid, is supposed to exist in the aqueous solution of CO_2; but this also readily loses water, yielding the true anhydride, $CO_2(=CO(OH)_2-H_2O)$. *Orthosulphuric acid*, $S(OH)_6$, probably exists in an aqueous solution of sulphuric acid, for the maximum contraction which occurs when H_2SO_4 and H_2O are mixed takes place when the proportion of acid to water is expressed by the formula $H_2SO_4.2H_2O$ or H_6SO_6. It very readily loses water, however, when heated, and if the evaporated solution be cooled to 8° C. the anhydro-acid, $SO(OH)_4$ or $H_2SO_4.H_2O$, crystallises, which in its turn loses water when heated, becoming the most stable anhydro-acid of sulphur, H_2SO_4 or $SO_2(OH)_2$. The solution of SO_3 in $H_2SO_4(H_2S_2O_7)$, which melts at 35° C. and is called anhydrosulphuric acid, must be regarded as a further anhydride of sulphuric acid—

$$\left.\begin{matrix}SO_2(OH)_2\\SO_2(OH)_2\end{matrix}\right\} - H_2O = \begin{matrix}S\\S\end{matrix}\!\!\begin{matrix}\diagup O_2(OH)\\O\\\diagdown O_2(OH)\end{matrix}$$

Orthosilicic acid, $Si(OH)_4$, is believed to exist in solution (p. 278), but it very easily loses water, becoming the anhydro-acid, $SiO(OH)_2$, metasilicic acid. By the loss of water from several molecules of orthosilicic acid, anhydro-acids of complex type would be produced; thus—

$$\left.\begin{matrix}Si(OH)_4\\Si(OH)_4\\Si(OH)_4\end{matrix}\right\} - 2H_2O = \begin{matrix}Si\\Si\\Si\end{matrix}\!\!\begin{matrix}\diagup (OH)_3\\O\\\diagup\diagdown (OH)_2\\O\\\diagdown (OH)_3\end{matrix}$$

The mineral silicates are undoubtedly derived from such complex silicic acids, the existence of which is, in many cases, also indicated by the isolation of acid chlorides (p. 191) corresponding with them.

Orthoboric acid, $B(OH)_3$, is well known. *Orthonitric acid*, $N(OH)_5$, is not known; ordinary nitric acid is the anhydro-acid $NO_2(OH)$.

The ortho-acid of chlorine should be $Cl(OH)_7$, for this element is probably heptavalent to elements other than hydrogen; but no anhydro-acid intermediate between this and $ClO_3(OH)$, perchloric acid, is known. *Orthoiodic acid*, $I(OH)_7$, is unknown; periodic acid, $IO(OH)_5$, is the first anhydro-acid from orthoiodic acid.

On reviewing the highest oxy-acids of the non-metallic elements, it will be found to be generally true that those acids are the most stable which contain the same

number of hydroxyl groups in the molecule as there are hydrogen atoms in the highest hydrogen compound of the element.

Phosphides of Hydrogen.

156. Although phosphorus and hydrogen do not combine directly, there are three compounds of these elements producible by processes of substitution, viz., PH_3, gas; P_2H_4, liquid; P_4H_2, solid.

Gaseous hydrogen phosphide, or phosphoretted hydrogen, or phosphine ($PH_3 = 34$ parts by weight), is by far the most important of these. It has been mentioned above as produced by the action of heat upon phosphorous acid, and when prepared by this process, it is a colourless gas, with a most powerful odour of putrid fish, inflaming on the approach of a light, and burning with a brilliant white flame, producing thick clouds of phosphorus pentoxide. It is slightly heavier than air (sp. gr. 1.18), and has been liquefied at $-90°$ C. and solidified at $-133°$ C.; it boils at $-85°$.

The ordinary method of preparing this gas for experimental purposes consists in boiling phosphorus with a strong solution of potash, when water is decomposed, its hydrogen combining with one part of the phosphorus, and its oxygen with another part forming hypophosphorous acid, which unites with the potash—

$$P_4 + 3KOH + 3H_2O = PH_3 + 3PH_2O(OK).$$

A few fragments of phosphorus are introduced into a small retort (Fig. 187), which is then nearly filled with a strong solution of potash (45 grams of stick potash in 100 c.c. of water), and heated. The extremity of the neck of the retort should not be plunged under water until the spontaneously inflammable gas is seen burning at the orifice, and the retort must not be placed close to the face of the operator, since explosions sometimes happen in preparing the gas, and the boiling potash produces dangerous effects. The gas may be collected in small jars filled with water, taking care that no bubble of air is left in them. It contains hydrogen phosphide mixed with free hydrogen, the latter being formed from the de-oxidation of water by the potassium hypophosphite. As each bubble of this gas escapes into the air through the water of the pneumatic trough, it burns with a vivid white flame, producing beautiful wreaths of smoke (phosphoric anhydride), resembling the *gunner's rings* sometimes seen in firing cannon. Small bubbles sometimes escape without spontaneously inflaming. If a bubble be sent up into a jar of oxygen, the flash of light is extremely vivid, and the jar must be a strong one to resist the concussion. It is advisable to add a trace of chlorine to the oxygen, to ensure the inflammation of each bubble, for an accumulation of the gas would shatter the jar.

Fig. 187.
Preparation of phosphoretted hydrogen.

It is stated that phosphoretted hydrogen may be added to pure oxygen without ignition until the pressure is reduced, when explosion suddenly occurs (compare the phenomenon of phosphorescence, p. 251).

If the phosphoretted hydrogen be passed through a tube cooled in a freezing-mixture of ice and salt, the gas escaping from the tube is found to have lost its spontaneous inflammability, although it takes fire on contact with flame. The cold tube contains the *liquid hydrogen phosphide* (P_2H_4), which was present in the gas in the state of vapour, and caused its spontaneous inflammability, for as soon as the liquid comes in contact with air it takes fire. When exposed to light, the

liquid phosphide is decomposed into the gaseous phosphide, and a yellow *solid phosphide* (P_4H_2), which is not spontaneously inflammable; $5P_2H_4 = P_4H_2 + 6PH_3$. It is for this reason that the spontaneously inflammable gas loses that property when kept (unless in the dark), depositing the solid phosphide upon the sides of the jar.

By passing a few drops of oil of turpentine up through the water into a jar of the spontaneously inflammable gas, this property will be entirely destroyed.

Hydrogen phosphide, when passed through solutions of some of the metals, precipitates their phosphides. For example, with cupric sulphate it gives a black precipitate of cupric phosphide; $3CuSO_4 + 2PH_3 = 3H_2SO_4 + P_2Cu_3$.

When this black precipitate is heated with solution of potassium cyanide, it evolves self-lighting hydrogen phosphide.* In fact, this is one of the easiest and safest methods of preparing this gas; for the cupric phosphide is readily obtained by simply boiling phosphorus in a solution of cupric sulphate.

Phosphine is absorbed by strong sulphuric acid, and, after a time, acts upon it with great evolution of heat, SO_2 being formed and sulphur deposited. Sulphur decomposes it in sunshine; $2PH_3 + S_6 = P_2S_3 + 3H_2S$.

The spontaneously inflammable hydrogen phosphide may also be obtained by throwing fragments of *calcium phosphide* into water; this substance is prepared by passing vapour of phosphorus over red-hot quicklime, or simply by heating small lumps of quicklime to bright redness in a crucible and throwing in fragments of phosphorus, closing the crucible immediately. The dark brown mass thus obtained is a mixture of pyrophosphate and phosphide of calcium, of somewhat variable composition. The calcium phosphide has been used in life-buoys for indicating by the flare their position on the water.

Phosphine has great pretensions to rank as the chemical analogue of ammonia, for although it has no alkaline properties, it is capable of combining with hydrobromic and hydriodic acids to form crystalline compounds such as *phosphonium iodide*, PH_4I, analogous to ammonium bromide and iodide; these compounds, however, are decomposed by water. It will be seen hereafter, that when the hydrogen in phosphine is displaced by certain compound radicles, such as ethyl, powerful organic bases are produced.

When phosphine is decomposed by a succession of electric sparks, 2 volumes of the gas yield 3 volumes of hydrogen, the phosphorus being deposited in the red form.

157. Two **chlorides of phosphorus** are known. The *trichloride* or *phosphorous chloride* (PCl_3), the acid chloride of phosphorous acid, is prepared by acting upon phosphorus with perfectly dry chlorine in the apparatus employed (p. 242) for preparing the chloride of sulphur. Red phosphorus may be used, and the product redistilled with a little vitreous phosphorus to decompose any PCl_5. Phosphorous chloride distils over very easily (boiling-point, 76° C.), as a colourless, pungent liquid (sp. gr. 1.61), which fumes strongly in air, its vapour decomposing the moisture of the air and producing hydrochloric acid fumes. In contact with water the liquid is immediately decomposed, yielding hydrochloric and phosphorous acids, as described for the preparation of the latter acid (p. 251). Its analogy to phosphorous anhydride is shown by its absorbing oxygen when boiled in the presence of that gas, and forming the *phosphorus oxychloride* or *phosphoryl chloride* $POCl_3$, the acid chloride of phosphoric acid. It also absorbs chlorine with avidity, becoming converted into *pentachloride of phosphorus* or *phosphoric chloride* (PCl_5). This compound, however, is more conveniently prepared by passing chlorine through a solution of phosphorus in carbon disulphide, carefully cooled. On evaporation, the pentachloride of phosphorus is deposited in white prismatic crystals, which volatilise below 100° C., and fume when exposed to air, from the production of hydrochloric acid. When PCl_5 is heated above 148° C. it is dissociated into PCl_3 and Cl_2, but this may be prevented by volatilising it in an atmosphere of PCl_3, and thus its vapour density has been determined. When thrown into water, it is decomposed into phosphoric and hydrochloric acids; $PCl_5 + 4H_2O = H_3PO_4 + 5HCl$. But if it be allowed to deliquesce in air, only a

* Cupric cyanide and potassium phosphide being formed, and the latter decomposed by water, giving hydrogen phosphide and potassium hypophosphite.

partial decomposition occurs, and the phosphorus oxychloride is formed; $PCl_5 + H_2O = POCl_3 + 2HCl$. The same compound is obtained by distilling P_2O_5 with NaCl; $2P_2O_5 + 3NaCl = POCl_3 + 3NaPO_3$.

This oxychloride may also be produced by heating phosphoric chloride with phosphoric anhydride; $P_2O_5 + 3PCl_5 = 5POCl_3$. A more instructive method of preparing it consists in distilling the phosphoric chloride with crystallised boric acid; $3PCl_5 + 2B(OH)_3 = 3POCl_3 + 6HCl + B_2O_3$.

Some of the organic acids (succinic, for example) may be converted into anhydrides, as the boric acid is in this case, by distilling with phosphoric chloride. The phosphorus oxychloride distils over (boiling-point, 107° C.) as a heavy (sp. gr. 1.7) colourless fuming liquid of pungent odour. Of course, it is decomposed by water, yielding hydrochloric and phosphoric acids. It will be found of the greatest use in effecting certain transformations in organic substances.

Pyrophosphoryl chloride, $P_2O_3Cl_4$, the acid chloride of pyrophosphoric acid, is a product of the action of NO_2 on PCl_3. It is a fuming liquid.

The analogy between water and hydrosulphuric acid would lead to the expectation that a *sulphochloride of phosphorus* or *thiophosphoryl chloride* ($PSCl_3$), corresponding with the oxychloride, would be formed by the action of hydrosulphuric acid upon phosphoric chloride; $PCl_5 + H_2S = PSCl_3 + 2HCl$. It is a colourless fuming liquid (boiling-point 125° C., sp. gr. 1.68), which is slowly decomposed by water, giving phosphoric, hydrochloric, and hydrosulphuric acids; $PSCl_3 + 4H_2O = H_3PO_4 + 3HCl + H_2S$. When attacked by solution of soda, it loses its chlorine to the sodium, and acquires the equivalent of oxygen, a sodium *thiophosphate* ($Na_3PO_3S.12H_2O$) being deposited in crystals. This salt evidently corresponds in composition with sodium orthophosphate ($Na_3PO_4.12H_2O$), and its production is expressed by the equation—$PSCl_3 + 6NaOH = 3NaCl + Na_3PO_3S + 3H_2O$. Salts of similar composition may be obtained with other metallic oxides.

The *bromides* and *oxybromide of phosphorus* correspond with the chlorine compounds; as also do the *fluorides*. The latter are gaseous under ordinary conditions.

Iodine in the solid state combines very energetically with phosphorus, but if the two elements be brought together in a state of solution in carbon disulphide, a more moderate action ensues, and two *iodides of phosphorus* may be obtained in crystals; a *tri-iodide* (PI_3) corresponding with the trichloride, and *phosphorus di-iodide* (P_2I_4), which has no analogue either among the oxygen, chlorine, or bromine compounds of phosphorus. P_2I_4 forms orange-red crystals, which are decomposed by water, with separation of red phosphorus; $3P_2I_4 + 12H_2O = 12HI + P_2 + 4P(OH)_3$.

The addition of a very small quantity of iodine to ordinary phosphorus, fused in a flask filled with carbonic acid gas, materially accelerates its conversion into the red modification, and allows the change to be effected at a much lower temperature than that required when the phosphorus is heated alone, probably because successive portions of vitreous phosphorus combine with the iodine to form an unstable iodide, which is in turn decomposed by the heat into red phosphorus and iodine.

158. The **sulphides of phosphorus** may be formed by the direct combination of their elements. Yellow phosphorus liquefies when mixed with sulphur (an operation not unattended by danger), and the liquid dissolves as much as 25 per cent. of sulphur. It fumes in air and readily ignites, but it appears to be only a solution of sulphur in phosphorus, which, like most other solutions, has a lower melting-point than that of the solvent (phosphorus). When a mixture of red phosphorus and sulphur is heated, combination occurs, and either P_2S_3 or P_2S_5 is formed according to the proportions used. A clay crucible is heated by a bunsen burner and a mixture of red phosphorus (31 parts) and sulphur (48 parts) is added by degrees, the crucible being covered after each addition until the reaction is over. The crucible is allowed to cool until the mass is about to solidify, and the *phosphorus trisulphide* is then poured on to an iron plate. It is a dirty yellow crystalline mass of sp. gr. 2.0 and melting-point 167° C.

Phosphorus pentasulphide, P_2S_5, is similarly prepared and melts at 275° C. and boils at 530° C.; from CS_2 it separates in nearly colourless crystals. Both sulphides deliquesce in air, being decomposed into oxyacids of phosphorus with evolution of H_2S, and both are used in organic chemistry for substituting S for O.

P_2S_5 combines with alkali sulphides, forming *thiophosphates*; $3K_2S + P_2S_5 = 2K_3PS_4$.

159. **Amides.**—A general reaction between ammonia and an acid chloride is the production of the *amide* corresponding with the acid whose chloride is being treated. The amide of an acid contains NH_2 (amidogen) in place of the hydroxyl of the acid; the reaction may be regarded as consisting of an exchange of Cl for NH_2; thus, the action of ammonia on phosphoryl chloride produces the amide of "ortho-phosphoric acid," $PO(NH_2)_3$, called *phospho-triamide*. The change may be written $PO{\cdot}Cl_3 + 3NH_2{\cdot}H = PO(NH_2)_3 + 3HCl$, but it will not occur unless excess of ammonia be present to combine with the liberated HCl, so that the actual reaction is $POCl_3 + 6NH_3 = 3NH_4Cl + PO(NH_2)_3$.

When an amide is boiled with an acid or an alkali it reacts with the water, producing the acid from which it is derived, and ammonia. Such a *decomposition by water* is termed *hydrolysis*; $PO(NH_2)_3 + 3HOH = PO(OH)_3 + 3NH_3$.

If an acid be present the NH_3 will immediately become an ammonium salt. If an alkali be present the ammonia will be evolved and the alkali will combine with the phosphoric acid. If neither acid nor alkali be present the change will not proceed far.

If the sulphochloride, $PSCl_3$, be substituted for the oxychloride and treated with ammonia, the corresponding *sulphosphotriamide*, $PS(NH_2)_3$, is obtained.

The action of ammonia on phosphoric chloride yields *chlorophosphamide*, $PCl_3(NH_2)_2$; $PCl_5 + 2NH_3 = 2HCl + PCl_3(NH_2)_3$, and *phospham*, PN_2H, a white solid which is the analogue of hydrogen nitride, N_3H.

When chlorophosphamide is boiled with water, a very stable insoluble substance is obtained, which is *phosphodiamide*; $N_2H_4PCl_3 + H_2O = 3HCl + N_2H_3PO$ (*phospho-diamide*).

When heated, it evolves ammonia and becomes *phosphonitrile*, the analogue of nitrous oxide; $N_2H_3PO = NH_3 + NPO$.

The phosphamides may be regarded as being derived from the ammonium ortho-phosphates by the abstraction of $3H_2O$; thus—

$(NH_4)_3PO_4$ *minus* $3H_2O$ = N_3H_3PO or $PO(NH_2)_3$, Phosphotriamide.
$(NH_4)_2HPO_4$ „ „ = N_2H_3PO or $PO(NH_2)NH$, Phosphamide-imide.
$NH_4H_2PO_4$ „ „ = NPO, Phosphonitrile.

Nitrogen chlorophosphide, $N^v_3P'''_3Cl_6$, is obtained by distilling phosphoric chloride with ammonium chloride; $3PCl_5 + 3NH_4Cl = N_3P_3Cl_6 + 12HCl$. It forms colourless rhombic prisms, melting at 114° C. and insoluble in water, but slowly decomposed by it; $2P_3N_3Cl_6 + 15H_2O = 12HCl + 3P_2O_3(NH_2)_2(OH)_2$, *pyrophosphodiamic acid*, or pyrophosphoric acid, $P_2O_3(OH)_4$, in which two NH_2 groups have been substituted for two OH groups.

ARSENIC.

As = 74.5 parts by weight.*

160. This element is often classed among the metals, because it has a metallic lustre and conducts electricity, but it is not capable of forming a base with oxygen, and the chemical character and composition of its compounds connect it in the closest manner with phosphorus.

In its mode of occurrence in nature it more nearly resembles the sulphur group of elements, for it is occasionally found in the uncombined state (*native arsenic*), but far more abundantly in combination with various metals, forming *arsenides*, which frequently accompany the sulphides of the same metals. The following are some of the chief arsenides and *arsenio-sulphides* found in the mineral kingdom:—

* The specific gravity of the vapour of arsenic, like that of phosphorus, indicates that 74.5 parts by weight only occupy half a volume. Hence the molecule of arsenic must be represented as $As_4 = 2$ volumes; but at very high temperatures a disposition to conform with the law is shown by a diminution in the vapour density.

Kupfernickel	$NiAs$	Mispickel or Arsenical pyrites	$FeS_2.FeAs_2$
Arsenical nickel	$NiAs_2$	Cobalt-glance	$CoS_2.CoAs_2$
Tin-white cobalt	$CoAs_2$	Nickel-glance	$NiS_2.NiAs_2$
Arsenical iron	Fe_2As_3		

But arsenic also occurs, like the metals, in combination with sulphur; thus we have red orpiment or realgar, As_2S_2, and yellow orpiment, As_2S_3. It is from these minerals that arsenic derives its name (*ἀρσενικόν, orpiment*).

The sulphides of arsenic are also found in combination with other sulphides; thus *Proustite* is a compound of the sulphides of silver and arsenic ($3Ag_2S.As_2S_3$); *Tennantite* contains sulphide of arsenic combined with the sulphides of iron and copper; and *grey copper ore* is composed of sulphide of arsenic with sulphides of copper, silver, zinc, iron, and antimony. In an oxidised form arsenic is found in *condurrite*, which contains arsenious anhydride (As_4O_6) and cuprous oxide. *Cobalt-bloom* consists of cobalt arsenate, $Co_3(AsO_4)_2$.

Arsenical pyrites is one of the principal sources of arsenic and its compounds, though a considerable quantity is also obtained in the form of arsenious oxide as a secondary product in the working of certain ores, especially those of copper, tin, cobalt, and nickel.

The substance used in the arts under the name of arsenic is really the arsenious oxide (As_4O_6); pure arsenic itself has very few useful applications, so that it is not the subject of an extensive manufacture. Arsenic can be extracted from *mispickel* ($Fe_2S_2As_2$) by heating it in earthern cylinders fitted with iron receivers in which the arsenic condenses as a metallic-looking crust, the heat expelling it from the mineral in the form of vapour.

On a small scale it may be obtained by heating a mixture of white arsenic with half its weight of recently calcined charcoal in a crucible (Fig. 188), the mixture being covered with two or three inches of charcoal in very small fragments, and the crucible so placed that this charcoal may be heated to redness first, in order to ensure the reduction of any oxide which might escape from below. In order to collect the arsenic, another crucible, having a small hole drilled through the bottom for the escape of gas, is cemented on to the first, in an inverted position, with fire-clay, and protected from the fire by an iron plate with a hole in it for the crucible. The reduction of arsenious anhydride by charcoal is thus represented—$As_4O_6 + C_6 = As_4 + 6CO$.

Fig. 188.—Extraction of arsenic.

For the sake of illustration, a small quantity of arsenic may be prepared from white arsenic by a method commonly employed in testing for that substance. A small tube of German glass is drawn out to a narrow point (A, Fig. 189), and sealed with the aid of the blow-pipe. A very minute quantity of white arsenic is introduced into the point of the tube, and a few fragments of charcoal are placed in the tube itself at B. The charcoal is heated to redness with a blow-pipe flame, and the point is then heated so as to drive the white arsenic in vapour over the red-hot charcoal, when a shining black ring of arsenic (C) will be deposited upon the cooler portion of the tube.

The arsenic thus obtained is a brittle mass of a dark steel-grey colour and brilliant metallic lustre (sp. gr. 5.7). It vaporises at 180° C. without melting unless it is heated in a sealed tube under the pressure of its own vapour, when it melts at 480° C. It is not changed by exposure to air, unless powdered and moistened, when it is slowly

converted into As_4O_6. When heated in air it oxidises rapidly at about 71° C., giving off white fumes of arsenious oxide and a characteristic garlic odour (recalling that of phosphorus), which is also produced when arsenical pyrites is struck with a hammer or pick. At a red heat it burns in air with a bluish-white flame, and in oxygen with great brilliancy. It is not dissolved by water or any simple solvent, but is oxidised and dissolved by nitric acid.

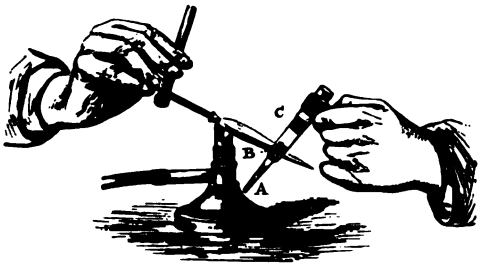


Fig. 189.—Reduction of arsenious oxide.

In its chemical relations to other elements, arsenic much resembles phosphorus, undergoing spontaneous combustion in chlorine, and easily combining with sulphur. Like phosphorus also, it combines with many metals, even with platinum, to form arsenides, and its presence often affects materially the properties of the useful metals.

Pure arsenic does not produce symptoms of poisoning till a considerable period after its administration, being probably first oxidised in the stomach and intestines, and converted into arsenious acid.

Arsenic vapour is colourless, but when rapidly cooled it appears yellow owing to the condensation of a cloud of minute yellow crystals which are an allotropic modification of arsenic, soluble in CS_2 and remarkably sensitive to light, which converts it into the black variety.

When arsenic is sublimed in a tube filled with hydrogen, ordinary or crystalline arsenic condenses on the warmer part of the tube, but on the cooler part, *amorphous arsenic* is deposited, of sp. gr. only 4.7. This is not so easily oxidised in moist air as the crystalline variety. At 360° C. it evolves heat and becomes converted into crystalline arsenic.*

161. **Oxides of Arsenic.**—Arsenic forms two oxides, corresponding with phosphorous and phosphoric anhydrides, viz., As_4O_6 and As_2O_5.

Arsenious oxide ($As_4O_6 = 396$ parts by weight)—Unlike phosphorus, arsenic, when burning in air, only combines with oxygen to form its lower oxide. Arsenious oxide, or *white arsenic*, is a very useful substance in many branches of industry. It is employed in the manufacture of glass, and of several colouring-matters. A large quantity is also consumed for the preparation of arsenic acid and arsenate of soda; it is, indeed, the source from which nearly all the compounds of arsenic are procured. Small quantities of crystalline arsenious oxide are occasionally found associated with the ores of nickel and cobalt.

White arsenic is manufactured by roasting the arsenical pyrites, chiefly obtained from the mines of Silesia, in *muffles* or ovens, through which air is allowed to pass, when the arsenic is converted into As_4O_6, and the sulphur into SO_2, which are conducted into large chambers wherein the As_4O_6 is deposited as a very fine powder. The iron of the

* Another amorphous variety of arsenic has been described as a brownish-black powder of sp. gr. 3.7. Doubt has been expressed concerning the amorphous character of this allotrope of arsenic.

pyrites is left partly as oxide, and partly as sulphate of iron. The removal of the As_4O_6 from the condensing-chambers is a very unwholesome operation, owing to its dusty and very poisonous character. The workmen are cased in leather, and protect their mouths and noses with damp cloths, so as to avoid inhaling the fine powder.

This rough white arsenic is subjected to a second sublimation on a smaller scale in iron vessels, when it is obtained in the form of a semi-transparent glassy mass known as *vitreous arsenious acid*, which gradually becomes opaque from crystallisation when kept, and ultimately resembles porcelain. The white arsenic sold in the shops is a fine powder, dangerously resembling flour in appearance, but so much heavier (sp. gr. 3.7) that it ought not to be mistaken for it. When examined under the microscope it appears in the form of irregular glassy fragments, mixed with octahedral crystals. White arsenic softens when gently heated, but does not fuse (unless in a sealed tube), being converted into vapour at 193° C., and depositing in brilliant octahedral crystals upon a cool surface. The experiment may be made in a small tube sealed at one end, the upper part of which should be slightly warmed before heating the arsenious oxide, so as to prevent too rapid condensation, which is unfavourable to the formation of distinct crystals. The octahedra are best examined with a binocular microscope. By saturating a boiling solution of KOH with As_4O_6, and allowing the liquid to cool, prismatic crystals (sp. gr. 4) separate. Thus As_4O_6 is both amorphous and dimorphous, the *amorphous* form (sp. gr. 3.7) being condensed from the vapour on a hot surface, the *octahedral* (sp. gr. 3.7) condensing on a cool surface, and the *prismatic* crystallising as described above. When crystallised from water both the other forms become octahedral. The change from amorphous to crystalline arsenious oxide is attended by evolution of heat.

The amorphous and octahedral forms differ in solubility, one part of the former dissolving in 108 parts of water at 15° C., and one part of the crystalline in 355 parts. At the boiling-point these numbers become 30 and 46 respectively.

This common poison may fortunately be easily recognised by sprinkling it upon a red-hot coal, when a strong odour of garlic is perceptible, due to the reduction of the As_4O_6 by the heated carbon; the vapour of white arsenic, or that of arsenic, is itself inodorous. The sparing solubility of white arsenic in water is very unfavourable to its action as a poison, for, when thrown into ordinary liquids, it is dissolved in very small quantity, the greater part of it collecting at the bottom. Even when taken into the stomach in a solid state, its want of solubility delays its operation sufficiently to give a better chance of antidotal treatment than in the case of most other common poisons. Its comparative insolubility is shown by its being almost tasteless. Although so little as 2.5 grains of white arsenic have been known to prove fatal, the exhibition of gradually increasing doses will so inure the system to the poison that comparatively large quantities can be administered at frequent intervals. When exhibited in this manner, white arsenic appears to have a remarkable effect on the animal body. Grooms occasionally employ it to improve the appearance of horses, and in Styria, it seems, it is taken by men and women for the same purpose, apparently favouring the secretion of fat. It is said that a continuance of the

custom develops a craving for this drug, and enables it to be taken without immediate danger, though the ultimate consequences are very serious. The antidote to the poison is ferric hydroxide, made by mixing magnesia with ferric chloride solution; this acts by rendering the arsenic insoluble.

The very general distribution of arsenic through the mineral kingdom makes it necessary that the analyst should ever be on the watch for this insidious poison. As has been already seen the arsenic in ordinary pyrites finds its way into the sulphuric acid made therefrom, and then into the commercial hydrochloric acid distilled with aid of this sulphuric acid. The use of sulphuric acid containing arsenic for converting starch into glucose subsequently used in making beer has been the cause of many deaths in the district consuming the beer. This beverage appears to be liable also to contain arsenic derived, it is alleged, from pyrites in the fuel used to dry the malt, from which the beer is brewed.

When thrown into water, white arsenic exhibits great repulsion for the particles of that liquid, and collects in a characteristic manner round little bubbles of air forming small white globes which are not wetted by the water. Even if stirred, with the water, and allowed to remain in contact with it for some hours, a pint of water (20 oz.) would not take up more than 20 grains. If boiling water be poured upon powdered white arsenic, and allowed to remain in contact with it till cold, it will dissolve about $\frac{1}{110}$th of its weight (22 grains in a pint).

When powdered white arsenic is boiled with water for two or three hours, 100 parts by weight of water may be made dissolve 11.5 parts, and when the solution is allowed to cool, about 9 parts will be deposited in octahedral crystals, leaving 2.5 parts dissolved in 100 of water (219 grains in a pint).

This great increase in the solubility of the arsenious oxide by long boiling with water is usually attributed to the conversion of the opaque or crystalline variety, which always composes the powder, into the vitreous modification, which is the more soluble in water (4 parts in 100 of water). Water, heated with white arsenic in a sealed tube, may be made to dissolve its own weight of it; as the solution cools, it first deposits prismatic crystals, and afterwards the ordinary octahedral form. The solution is very feebly acid to blue litmus-paper. Glycerine dissolves As_4O_6 easily when heated.

White arsenic dissolves abundantly in hot hydrochloric acid (a part of it being converted into arsenious chloride), and as the solution cools, part of the oxide is deposited in large octahedral crystals. The formation of these crystals is attended by flashes of light, visible in a darkened room.

This experiment, which is exceedingly beautiful, is best performed by boiling 60 grains of arsenious oxide in 500 c.c. of a mixture of equal volumes of strong hydrochloric acid and water in a flask, and allowing the solution to cool slowly; after a time the crystals begin to form, a flash of light accompanying the formation of each, and the effect may be enhanced by carefully shaking the flask. It is said that it is only the vitreous form which exhibits this phenomenon; but the same solution will generally serve for the above experiment any number of times if it be reheated, although the arsenious oxide has, of course, been deposited in the crystalline form; it is, however, remarkable that the experiment sometimes unaccountably fails.

Solutions of the alkalies readily dissolve arsenious oxide, forming alkali arsenites, the solutions of which are capable of dissolving arsenious oxide more easily than water can, and deposit it in crystals on cooling (see above). On adding a small quantity of hydrochloric acid to the solution of the alkali arsenite, a white precipitate of arsenious oxide is formed.

White arsenic has the property of preventing the putrefaction of skin

and similar substances, and is occasionally employed for the preservation of objects of natural history, &c.

Arsenites.—Arsenious acid, properly so called, has not yet been obtained in the separate state. The aqueous solution of white arsenic, when neutralised exactly with ammonia, yields, with silver nitrate, a yellow precipitate having the composition Ag'_3AsO_3; with cupric sulphate, a green precipitate having the composition $Cu''HAsO_3$; with zinc sulphate, a white precipitate containing $Zn''_3(AsO_3)_2$; and with magnesium sulphate, a white precipitate of $Mg''HAsO_3$. It would appear, therefore, that the *arsenious acid* from which these salts are derived is a tribasic acid having the formula H_3AsO_3, or $As(OH)_3$, corresponding with boric acid, H_3BO_3. Arsenious acid does not destroy the alkaline reaction of the alkalies, and it does not decompose the alkaline carbonates unless heat is applied, proving it to be a feeble acid. The ammonium arsenite is very unstable, evolving ammonia freely when exposed to the air. When arsenious oxide is dissolved in a hot solution of ammonia, octahedral crystals of it are deposited on cooling, notwithstanding the presence of ammonia in large excess. The alkali arsenites are more correctly *metarsenites*, for they are derived from $HAsO_2$, or $AsO(OH)$, metarsenious acid; the potassium arsenite is $KAsO_2$.

When the carbonates of potassium and sodium are fused with an excess of arsenious oxide, brilliant transparent glasses are obtained which are similar in composition to glass of borax ($K_2As_4O_7$ and $Na_2As_4O_7$).

If an alkali arsenite be fused in contact with platinum, the latter is easily melted, combining with a small proportion of arsenic to form a fusible platinum arsenide, a portion of the arsenite being converted into arsenate. The alkali arsenates (from arsenic acid, H_3AsO_4) are so much more stable than the arsenites that the latter exhibit a great tendency to pass into the former, with separation of arsenic.

The arsenites of potassium and sodium in solution are sometimes employed as sheep-dipping compositions; and an arsenical soap, composed of potassium arsenite, soap, and camphor, is used by naturalists to preserve the skins of animals. Sodium arsenite is also occasionally employed for preventing incrustations in steam boilers, being prepared for that purpose by dissolving 2 molecules of white arsenic and 1 molecule of sodium carbonate.

Scheele's green is an arsenite of copper ($CuHAsO_3$) prepared by dissolving white arsenic in a solution of potassium carbonate, and decomposing the arsenite of potassium thus produced by adding sulphate of copper, when the arsenite of copper is precipitated. This poisonous colour is used to impart a bright green tint to paper hangings, and is sometimes injurious to the health of the occupants of rooms thus decorated, since the arsenite of copper is often easily rubbed off the paper, and diffused through the air in the form of a fine dust, a small portion of which is inhaled with every breath.

The presence of the arsenite of copper in a sample of such paper is readily proved by soaking it in a little ammonia, which will dissolve the arsenite of copper to a blue liquid, the presence of arsenic in which may be shown by acidifying it with a little pure hydrochloric acid, and boiling with one or two strips of pure copper, which will become covered with a steel-grey coating of arsenide of copper. On washing the copper, drying it on filter-paper, and heating it in a small tube (Fig. 190), the arsenic will be converted into arsenious oxide, which will deposit in brilliant octahedral crystals on the cool part of the tube. It is obvious that, to avoid mistakes, the ammonia, hydrochloric acid, and copper should be examined in precisely the same way, without the suspected paper, so as to render it certain that the arsenic is not derived from them.

The effective green colour of the arsenite of copper also leads to its

employment as a colour for feathers, muslin, &c., where it is very injurious to the health of the workpeople. It has even been ignorantly or recklessly used for colouring twelfth-cake ornaments, &c.

Emerald-green (Paris green) is a combination of arsenite and acetate of copper obtained by mixing hot solutions of equal weights of white arsenic and acetate of copper. Solution of potassium arsenite (*Fowler's solution*) has long been used in medicine.

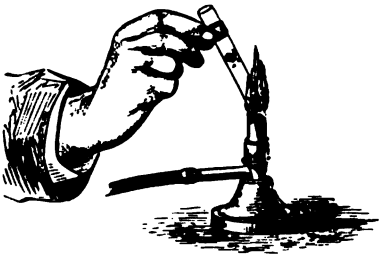


Fig. 190.

Both Scheele's green and Paris green are used as insecticides on growing crops.

162. **Arsenic acid** (H_3AsO_4 or $AsO(OH)_3$). Arsenic acid is prepared by oxidising white arsenic with three-fourths of its weight of nitric acid of sp. gr. 1.35, when it dissolves with evolution of much heat and abundant red fumes of nitrous anhydride—

$$As_4O_6 + 4HNO_3 + 4H_2O = 2N_2O_3 + 4H_3AsO_4.$$

After cooling, the solution deposits very deliquescent prismatic crystals containing $2H_3AsO_4.H_2O$. When heated to 100° C., these melt, and the liquid deposits needle-like crystals of *ortho-arsenic acid*, H_3AsO_4, corresponding with orthophosphoric; at 180° C., $2H_3AsO_4 = H_2O + H_4As_2O_7$, *pyro-arsenic acid*, corresponding with pyrophosphoric; at 206° C., $H_4As_2O_7 = H_2O + 2HAsO_3$, *metarsenic acid*, corresponding with metaphosphoric; but here the resemblance ceases, for at 260° C., $2HAsO_3 = H_2O + As_2O_5$, whereas HPO_3 may be vaporised without decomposition. When metarsenic and pyro-arsenic acids are dissolved in water, they at once become ortho-arsenic acid. The meta- and pyro-arsenates are known only in the solid state. As_2O_5 is decomposed at a red heat into As_4O_6 and oxygen.

Arsenic anhydride, As_2O_5, has very much less attraction for water than has the phosphoric anhydride with which it corresponds; it deliquesces slowly in air, and dissolves rather reluctantly in water. Neither does it appear that its combinations with water differ from each other, like the phosphoric acids, in the salts to which they give rise, arsenic acid forming tribasic salts only, like common phosphoric acid. The arsenates correspond very closely with the orthophosphates, with which they are isomorphous (*i.e.*, identical in crystalline form). Thus the three arsenates of sodium are similar in composition to the three orthophosphates, the formulæ being $Na_3AsO_4.12Aq$; $Na_2HAsO_4.12Aq$; and $2(NaH_2AsO_4).Aq$.

The common arsenate of soda ($Na_2HAsO_4.7Aq$) is largely used by calico-printers as a substitute for the dung-baths formerly employed, since, like the common phosphate of soda, it possesses the feebly alkaline properties required in that particular part of the process. It is manufactured by combining arsenious oxide with soda, and heating the resulting arsenite with sodium nitrate, from which it acquires oxygen, becoming converted into sodium arsenate.

Calcium arsenate, $2CaHAsO_4.7H_2O$, has been found in crystalline crusts at Joachimsthal. *Arsenio-siderite* and *xantho-siderite* are calcium ferric arsenates.

Arsenic acid is used by the calico-printer as an acid and by the dye-stuff maker as an oxidant. It is a much more powerful acid than arsenious acid, being comparable, in this respect, with phosphoric acid. It is less stable than phosphoric acid, and acts as an oxidising agent. Sulphurous acid, which is without action on phosphoric, reduces arsenic acid to arsenious acid; $H_3AsO_4 + H_2SO_3 = H_3AsO_3 + H_2SO_4$.

163. **Arsenetted hydrogen, hydrogen arsenide, or *arsine*** (AsH_3 = 78 parts by weight).—The only compound of arsenic and hydrogen the existence of which has been satisfactorily established is that which corresponds with ammonia and phosphine. It is prepared by the action of sulphuric acid diluted with three parts of water upon the zinc arsenide, obtained by heating equal weights of zinc and arsenic in an earthern retort; $Zn_3As_2 + 3H_2SO_4 = 2AsH_3 + 3ZnSO_4$. The gas is so poisonous in its character that its preparation in the pure state is attended with danger. It has a sickly alliaceous odour, and may be liquefied at $-55°$ C. and solidified at $-113°$ C. It is inflammable, burning with a peculiar, livid flame, producing water and fumes of arsenious oxide; $4AsH_3 + O_{12} = As_4O_6 + 6H_2O$. The chief interest attaching to this gas depends upon the circumstance that its production allows of the detection of very minute quantities of arsenic in cases of poisoning.

The application of this test, known as *Marsh's test*, is the safest method of preparing arsenetted hydrogen in order to study its properties, for it is obtained so largely diluted with free hydrogen that it ceases to be so very dangerous. Some fragments of granulated zinc are introduced into a half-pint bottle (Fig. 191), provided with a funnel tube (A), and a narrow tube (B) bent at right angles and drawn out to a jet at the extremity; this tube should be made of German glass, so that it may not fuse easily. The bottle having been about one-third filled with water, a little diluted sulphuric acid is poured down the funnel-tube so as to cause a moderate evolution of hydrogen, and after about five minutes (to allow the escape of the air) the hydrogen is kindled at the jet. If a few drops of a solution obtained by boiling white arsenic with water be now poured down the funnel, arsenetted hydrogen will be evolved together with the hydrogen; $As_4O_6 + Zn_{12} + 12H_2SO_4 = 4AsH_3 + 12ZnSO_4 + 6H_2O$.

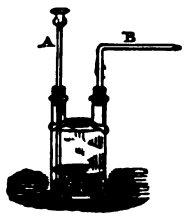


Fig. 191.

Fig. 192.

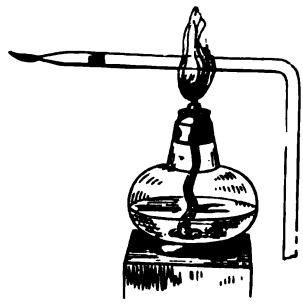


Fig. 193.

The hydrogen flame will now acquire the livid hue above referred to, and a white smoke of As_4O_6 will rise from it. If a piece of glass or porcelain be depressed upon the flame (Fig. 192), it will acquire a brown coating of arsenic, just as carbon would be deposited from an ordinary gas-flame. Arsenetted hydrogen is easily decomposed by heat (230° C.), so that if the glass tube through which it passes be heated with a spirit-lamp (Fig. 193) a dark *mirror* of arsenic will be deposited a little in front of the heated part, and the flame of the gas will lose its livid hue. These deposits of arsenic are extremely thin, so that a very minute quantity of

arsenic is required to form them, thus rendering the test one of extraordinary delicacy. It must be remembered, however, that both sulphuric acid and zinc are liable to contain arsenic, so that erroneous results may be very easily arrived at by this test.

An electrolytic test for arsenic may also be employed which depends upon the circumstance that when a fairly powerful galvanic current is passed through an acid liquid containing arsenic, arsenetted hydrogen is evolved at the negative terminal along with the hydrogen of the decomposed water.

Arsenetted hydrogen, like sulphuretted hydrogen, causes dark precipitates in many metallic solutions.

Silver nitrate is reduced to the metallic state by AsH_3; $AsH_3 + 6AgNO_3 + 3H_2O = H_3AsO_3 + 6HNO_3 + 3Ag_2$. A piece of filter-paper, spotted with silver nitrate solution, will have the spots blackened if held before the tube from which the gas issues. The simplest test for arsenic in wall-paper, &c., is to drop a piece of the paper into a glass containing some zinc and sulphuric acid, and to cover the mouth of the glass with a piece of paper wetted with silver nitrate, which will be blackened if arsenic be present. The purity of the materials should be tested first in the same way, and the absence of sulphur, which also blackens silver nitrate, should be proved by lead acetate, which is not blackened by arsenic.

Hydrogen phosphide, hydrogen arsenide, and ammonia constitute a group of hydrogen compounds having certain properties in common, which distinguish them from the compounds of hydrogen with other elements.

Two volumes of each of these gases contain three volumes of hydrogen.

They are all possessed of peculiar odours, that of ammonia being the most powerful and that of hydrogen arsenide the least. Ammonia is powerfully alkaline, phosphine exhibits some tendency to play an alkaline part, whilst arsine seems devoid of alkaline disposition. They are all inflammable, ammonia being the least so of the group, and are decomposed by heat, ammonia least easily, and hydrogen arsenide most easily. They are all producible from their corresponding oxygen compounds, viz., N_2O_3, P_4O_6, and As_4O_6, by the action of nascent hydrogen (*e.g.*, by contact with zinc and diluted sulphuric acid).

All three are the prototypes of various organic bases which contain some compound radicle in place of the hydrogen, thus—

NH_3 is the prototype of		triethylamine	$N(C_2H_5)_3$
PH_3	,,	triethylphosphine	$P(C_2H_5)_3$
AsH_3	,,	triethylarsine	$As(C_2H_5)_3$

164. **Arsenic trichloride, or arsenious chloride.**—Only one compound of chlorine with arsenic ($AsCl_3$) is well known.* The trichloride may be formed by the direct union of its elements, but the simplest laboratory process for procuring it consists in heating white arsenic in dry chlorine, in a tubulated retort (A, Fig. 194). The arsenious anhydride soon melts, and the trichloride distils, leaving a melted mass in the flask, which is a brilliantly transparent glass when cool; its composition varies somewhat with the temperature used, but appears to be essentially $As_4O_6.As_2O_5$. The same vitreous compound may be obtained by fusing arsenious and arsenic oxides together. The reaction may be represented by the equation—

$$11As_4O_6 + Cl_{24} = 8AsCl_3 + 6(As_4O_6.As_2O_5).$$

Arsenic trichloride bears a great general resemblance to phosphorus trichloride; it is a heavy (sp. gr. 2.2, b.p. 134° C.), pungent, fuming liquid, decomposed by the moisture of the air, its vapours depositing a white coating upon the objects in its immediate neighbourhood. When poured into water it deposits arsenious oxide; $4AsCl_3 + 6H_2O = As_4O_6 + 12HCl$; but when dissolved in the smallest possible quantity of water it deposits crystals of the formula AsOCl. H_2O or $AsCl(OH)_2$.

When white arsenic is dissolved in hydrochloric acid, arsenious chloride is formed, $As_4O_6 + 12HCl = 4AsCl_3 + 6H_2O$, and remains undecomposed by the water

* It is said that the pentachloride can be formed by the action of hydrochloric acid gas on As_2O_5 in presence of ether.

in the presence of strong hydrochloric acid, but if water be added, arsenious oxide is precipitated. When the solution in hydrochloric acid is distilled, the arsenious chloride distils over, and this is sometimes a convenient method of separating arsenic from articles of food, &c., in testing for that poison. When heated in dry hydrochloric acid gas, white arsenic yields a glassy compound, which contains $As_4O_6.2AsOCl$; $3As_4O_6 + 4HCl = 2(As_4O_6.2AsOCl) + 2H_2O$.

Fig. 194.

$AsCl_3$ and AsH_3 decompose each other, yielding 3HCl and As_2.

Arsenious bromide much resembles the chloride in its chemical characters, but is a solid crystalline substance, fusing at 25° C. and boiling at 220° C.

165. *Arsenic tri-iodide*, or *arsenious iodide* (AsI_3), is remarkable for not being decomposed by water, like the corresponding phosphorus compound. When obtained by heating together arsenic and iodine, it sublimes in brick-red flakes, which, if prepared on a large scale, hang in long laminæ, like sea-weed. It may be dissolved in boiling water, and crystallises unchanged. It may even be prepared by heating 3 parts of arsenic with 10 of iodine and 100 of water, when the solution deposits red crystals of the hydrated tri-iodide, from which the water may be expelled by a gentle heat.

AsI_3 is precipitated as a golden crystalline powder on mixing a hot solution of As_4O_6 in HCl with a strong solution of KI.

Arsenic di-iodide, AsI_2, is obtained by heating 1 part of arsenic and 2 parts of iodine in a sealed tube to 230° C., and crystallising from CS_2 in an atmosphere of CO_2. It forms red prismatic crystals which become black when treated with water, according to the equation $3AsI_2 = 2AsI_3 + As$.

When iodine is dissolved in a solution of arsenious acid, this is oxidised to arsenic acid; $H_2AsO_3 + H_2O + I_2 = H_3AsO_4 + 2HI$. When the solution is concentrated by evaporation, the change is reversed, and iodine liberated.

The *arsenic tri-fluoride* (AsF_3) resembles the trichloride, but is much more volatile (b.p. 63° C.) It may be obtained by distilling 4 parts of arsenious oxide with 5 of fluor spar and 10 of strong sulphuric acid, in a leaden retort (see p. 202). It does not attack glass unless water be present, which decomposes it into arsenious and hydrofluoric acids. PCl_5 converts it into FP_5 and $AsCl_3$.

166. **Sulphides of Arsenic.**—There are three well-known sulphides of arsenic, having the composition As_2S_2, As_2S_3, and As_2S_5, the two former being found in nature.

Realgar (As_2S_2) is a beautiful mineral, crystallised in orange-red prisms; but the *red orpiment* used in the arts is generally prepared by heating a mixture of white arsenic and sulphur, when sulphurous acid gas escapes, and an orange-coloured mass of realgar is left. Another process for preparing it consists in distilling arsenical pyrites with sulphur or with iron pyrites; $FeS_2.FeAs_2 + 2FeS_2 = 4FeS + As_2S_2$. The realgar distils, and condenses to a red transparent solid. Realgar burns in air with a blue flame, yielding arsenious and sulphurous oxides. If it be thrown into melted saltpetre, it burns with a brilliant white flame, being converted into arsenate and sulphate of potassium. This brilliant flame renders realgar an important ingredient in *Indian fire* and similar compositions for fireworks and signal lights. A mixture of one part of red orpiment with 3.5 parts of sublimed sulphur and 14 parts of nitre is used for signal light composition.

Realgar is not easily attacked by acids; nitric acid, however, dissolves it, with the aid of heat, forming arsenic acid and sulphuric acid, with separation of part

of the sulphur in the free state. Alkalies (KOH for example) partly dissolve it, leaving a dark brown substance, which appears to contain free arsenic; $3As_2S_2 = 2As_2S_3 + As_2$. When exposed to air realgar is partly oxidised and converted into a mixture of As_2S_2 and As_4O_6.

Yellow orpiment, or *arsenious sulphide* (As_2S_3), is found native in yellow prismatic crystals. The pigment known as *King's yellow* is a mixture of arsenious sulphide and arsenious anhydride, prepared by subliming excess of sulphur with white arsenic; $S_9 + As_4O_6 = 2As_2S_3 + 3SO_2$. It is, of course, very poisonous.

This substance, like realgar, is not much affected by acids, excepting nitric acid; but it dissolves entirely in potash, forming potassium arsenite and *thioarsenite*; $6KOH + As_2S_3 = K_3AsS_3 + K_3AsO_3 + 3H_2O$.* Ammonia also dissolves it easily, forming a colourless solution which is employed for dyeing yellow, since, if a piece of stuff be dipped into it and exposed to air, the ammonia will volatilise, leaving the yellow orpiment behind. When As_2S_3 is boiled with a strong solution of sodium carbonate, H_2S is evolved and As_2S_2 is deposited as a crystalline powder.

The formation of the characteristic yellow sulphide is turned to account in testing for arsenic; if a solution prepared by boiling white arsenic with distilled water be mixed with a solution of hydrosulphuric acid, a bright yellow liquid is produced, which looks opaque by reflected, but transparent by transmitted, light, and may be passed through a filter without leaving any solid matter behind. This solution probably contains a soluble *colloidal* form of arsenious sulphide; this is, however, rendered insoluble by evaporation. The addition of a little hydrochloric acid, or of sal-ammoniac, and many other neutral salts, will also cause a separation of the sulphide from this solution; even the addition of hard water will have that effect. If the solution of arsenious acid be acidified with hydrochloric acid before adding the hydrosulphuric acid, the bright yellow sulphide is precipitated at once, and may be distinguished from any other similar precipitate by its ready solubility in solution of ammonium carbonate.

Arsenic sulphide (As_2S_5) possesses far less practical importance than the preceding sulphides; it may be obtained by fusing As_2S_3 with sulphur, when it forms an orange-coloured glass, easily fusible, and capable of being sublimed without change. When hydrosulphuric acid gas is passed slowly through solution of arsenic acid, very little, if any, arsenic sulphide is formed, a white precipitate of sulphur being first obtained, the hydrogen reducing the arsenic acid to arsenious acid†; $H_3AsO_4 + H_2S = H_3AsO_3 + H_2O + S$; and if the passage of the gas be continued, the arsenious acid is decomposed, and arsenious sulphide is precipitated; these changes are much accelerated by heat. But a rapid current of H_2S passed through a solution of arsenic acid in presence of much free hydrochloric acid throws down pure arsenic sulphide. If a solution of sodium arsenate be saturated with H_2S, it is converted into sodium *thioarsenate*, Na_3AsS_4. On adding hydrochloric acid to this solution, a bright yellow precipitate of arsenic sulphide is obtained. *Cuprous sulpharsenate*, or *Clarite* (Cu_3AsS_4), is found in the Black Forest.

167. **Review of Nitrogen, Phosphorus, and Arsenic.**—These elements are connected together by the general analogy of their hydrogen and oxygen compounds, the two last members of the group being far more closely connected with each other than with nitrogen. With the metals they are connected through arsenic, the hydrogen-compound of which is very similar in properties, and probably in composition, to antimonetted hydrogen; arsenious oxide (As_4O_6) is also capable of occupying the place of antimonious oxide (Sb_4O_6) in certain salts of that oxide; and the sulphides of antimony correspond in composition, and in some of their properties, with those of arsenic. One form of

* Since the metarsenite, $KAsO_2$, is the only potassium arsenite which has been prepared, and the *metathioarsenite*, $KAsS_2$, appears to exist in the solution, the reaction is better expressed by the equation, $2As_2S_3 + 4KOH = KAsO_2 + 3KAsS_2 + 2H_2O$.

† Under some conditions the solution remains clear at first, sulphoxyarsenic acid being formed which is decomposed by more H_2S with precipitation of As_2S_5. (1) $H_3AsO_4 + H_2S = H_3AsO_3S + H_2O$; (2) $2H_3AsO_3S + 3H_2S = As_2S_5 + 6H_2O$.

arsenious oxide (the prismatic) is isomorphous with native oxide of antimony, and this oxide may be obtained in octahedra, the ordinary form of arsenious oxide, so that these oxides are *isodimorphous*.

These elements are also connected with the oxygen group through sulphur, selenium, and tellurium, the relations of which to hydrogen and the metals are somewhat similar to those of phosphorus and arsenic.

SILICON.

$Si^{IV} = 28.2$ parts by weight.

168. In many of its chemical relations to other bodies this element will be found to bear a great resemblance to carbon; but whilst carbon is the characteristic element of organic substances, silicon is the most abundant in the mineral world, where it is chiefly found in combination with oxygen, as silica (SiO_2), either alone or as *silicates*.

Silica ($SiO_2 = 60$ parts by weight).—The purest natural form of silica is the transparent and colourless variety of quartz known as *rock crystal*, the most widely diffused ornament of the mineral world, often seen crystallised in beautiful six-sided prisms, terminated by six-sided pyramids (Fig. 195), which are always easily distinguished by their great hardness, scratching glass almost as readily as the diamond. Coloured of a delicate purple, probably by a little organic matter, these crystals are known as *amethysts*; and when of a brown colour, as *Cairngorm stones* or *Scotch pebbles*. Losing its transparency and crystalline structure, we meet with silica in the form of *chalcedony* and of *carnelian*, usually coloured, in the latter, with oxide of iron.

Fig. 195.—Crystal of quartz.

Hardly any substance has so great a share in the lapidary's art as silica, for in addition to the above instances of its value for ornamental purposes, we find it constituting *jasper*, *agate*, *cat's eye*, *onyx*, so much prized for cameos, *opal*, and some other precious stones. In opal the silica is combined with water.

Sand, of which the whiter varieties are nearly pure silica, appears to have been formed by the disintegration of siliceous rocks, and has generally a yellow or brown colour, due to the presence of oxide of iron.

The resistance offered by silica to all impressions has become proverbial in the case of *flint*, which consists essentially of that substance coloured with some impurity. Flints are generally found in compact masses, distributed in regular beds throughout the chalk formation; their hardness, which even exceeds that of quartz, rendered them useful, before the days of matches, for striking sparks with steel; small particles of metal are thus detached, and are so heated by the percussion as to continue to burn (see p. 37) in the air, and to inflame tinder or gunpowder upon which they are allowed to fall.

The part taken by silica in natural operations appears to be chiefly a mechanical one, for which its stability under ordinary influences

peculiarly fits it, for it is found to constitute the great bulk of the soil which serves as a support and food-reservoir for land plants, and enters largely into the composition of the greater number of rocks.

But that this substance is not altogether excluded from any share in life, is shown by its presence in the shining outer sheath of the stems of the grasses and cereals, particularly in the hard external coating of the Dutch rush used for polishing, and in the joints of the bamboo, where it forms the greater part of the matter known as *tabasheer*. This alone would lead to the inference that silica could not be absolutely insoluble, since the capillary vessels of plants are known to be capable of absorbing only such substances as are in a state of solution. Many natural waters also present us with silica in a dissolved state, and often in considerable quantity, as, for example, in the geysers of Iceland, which deposit a coating of silica upon the earth around their borders.

Pure water, however, has no solvent action upon the natural varieties of silica. The action of an alkali is required to bring it into a soluble form.

To effect this upon the small scale, some white sand is very finely powdered (in an agate mortar), mixed with about four times its weight of dried sodium carbonate, placed upon a piece of platinum foil slightly bent up (Fig. 196), and fused by directing the flame of a blowpipe upon the under side of the foil. Effervescence will be observed, due to the escape of carbonic acid gas. The piece of platinum foil, when cool, may be placed in a little warm water, and allowed to soak for some time, when the melted mass will gradually dissolve, forming a solution of *sodium silicate*. This solution will be found decidedly alkaline to test-papers.

Fig. 196.—Fusion on platinum foil.

If a portion of the solution of sodium silicate in water be poured into a test-tube, and two or three drops of hydrochloric acid added to it, with occasional agitation, effervescence will be produced by the expulsion of any carbonic acid gas still remaining, and the solution will be converted into a gelatinous mass by the separation of silicic acid. But if another portion of the solution be poured into an excess of dilute hydrochloric acid (*i.e.*, into enough to render the solution distinctly acid), the silicic acid will remain dissolved in the water, together with the sodium chloride formed.

In order to separate the sodium chloride from the silicic acid, the process of *dialysis* * must be adopted.

Dialysis is the separation of dissolved substances from each other by taking advantage of the different rates at which they pass through moist diaphragms or *septa*. It is found that those substances which crystallise

* From διαλύω, to part asunder.

(*crystalloids*) and the mineral acids pass through such septa in a solution faster than do amorphous substances (*colloids*).

If the mixed solution of sodium chloride and silicic acid were poured upon an ordinary paper filter, it would pass through without alteration; but if parchment paper be employed, which is not pervious to water, although readily moistened by it, none of the liquid will pass through. If the cone of parchment paper be supported upon a vessel filled with distilled water (Fig. 197), so that the water may be in contact with the outer surface of the cone, the hydrochloric acid and the sodium chloride will pass through the substance of the parchment paper, and the water

Fig. 197.

Fig. 198.—Dialyser.

charged with them may be seen descending in dense streams from the outside of the cone. After a few hours, especially if the water be changed occasionally, the whole of the hydrochloric acid and sodium chloride will have passed through, and a pure solution of silicic acid in water will remain in the cone.

A convenient form of *dialyser* is represented in Fig. 198; it consists of parchment paper stretched over a gutta-percha ring and held in this position by a concentric ring. It is suspended on a surface of water and the solution to be dialysed is poured upon it.

This solution is believed to contain the *orthosilicic acid*, $H_2O.2SiO_2$, or H_4SiO_4, or $Si(OH)_4$. It is very feebly acid to blue litmus-paper, and not perceptibly sour to the taste. It has a great tendency to set into a jelly in consequence of the sudden separation of silicic acid. If it be slowly evaporated in a dish, it soon solidifies; but, by conducting the evaporation in a flask, so as to prevent any drying of the silicic acid at the edges of the liquid, it may be concentrated until it contains 14 per cent. of silicic acid. When this solution is kept, even in a stoppered or corked bottle, it sets into a transparent gelatinous mass, which gradually shrinks and separates from the water. When evaporated, *in vacuo*, over sulphuric acid, it gives a transparent lustrous glass which is composed of 22 per cent. of water and 78 per cent. of silica ($H_2O.SiO_2$). This is also the composition of the gelatinous precipitate produced by acids in the solution of sodium silicate. It is sometimes written H_2SiO_3 or $SiO(OH)_2$, and called *metasilicic acid.*

This behaviour of silicic acid is typical of colloids; they can generally exist in solution (the *hydrosol* form), but are apt to separate as a jelly (the *hydrogel* form) from such solutions. Gelatine is a familiar example.

The hydrated silica cannot be redissolved in water, and is only soluble to a slight extent in hydrochloric acid. If it be heated to expel the water, the silica which remains is insoluble both in water and in hydrochloric acid, but is dissolved when boiled with solution of potash or soda, or their carbonates.

Silica in the naturally crystallised form, as rock crystal and quartz,

is insoluble in boiling solutions of the alkalies, and in all acids except hydrofluoric; but amorphous silica (such as opal and *tripoli*) is readily dissolved by boiling alkalies. These represent, in fact, two distinct modifications of silica, which may be said to be *dimorphous*.* A transparent piece of rock crystal may be heated to bright redness without change, but if it be powdered previously to being heated, its specific gravity is diminished from 2.6 to 2.4, and it becomes soluble in boiling alkalies, having been converted into the amorphous modification. The natural forms of amorphous silica of sp. gr. 2.2 are always hydrated, and even some of the varieties of sp. gr. 2.6, such as flint, agate, and chalcedony, contain a little water, pointing to the aqueous origin of all silica.

Crystals of quartz have been obtained artificially by the prolonged action of water upon glass at a high temperature under pressure. When fused with the oxyhydrogen blowpipe, silica does not crystallise, being thus converted into the amorphous variety of sp. gr. 2.2, which may be worked while soft into threads and even tubes, much as glass is. The threads are useful in electrical apparatus on account of their excellent insulating property, far surpassing that of glass in a moist atmosphere. The tubes are useful on account of the high temperature and rapid changes of temperature they can withstand without fusion or fracture.

To prepare the amorphous modification of silica artificially, white sand in very fine powder may be fused, in a platinum crucible, with six times its weight of a mixture of equal weights of the potassium and sodium carbonates, the mixture being more easily fusible than either of the carbonates separately. The crucible may be heated over a gas burner supplied with a mixture of gas and air, or may be placed in a little calcined magnesia contained in a fire-clay crucible, which may be covered up and introduced into a good fire. The platinum crucible is never heated in direct contact with fuel, since the metal would become brittle by combining with carbon, silicon, and sulphur derived from the fuel. The magnesia is used to protect the platinum from contact with the clay crucible. When the action of the silica upon the alkali carbonates is completed, which will be indicated by the cessation of the effervescence, the platinum crucible is allowed to cool, placed in an evaporating dish, and soaked for a night in water, when the mass should be almost entirely dissolved. Hydrochloric acid is then added to the solution, with occasional stirring, until it is distinctly acid to litmus-paper. On evaporating the solution, it will, at a certain point, solidify to a gelatinous mass of hydrated silica, which would be ejected from the dish if evaporation over the flame were continued. To prevent this, the dish is placed over an empty iron saucepan so that the heat from the flame may be equally distributed over the bottom of the dish. When the mass is quite dry the dish is allowed to cool, and some water is poured into it, which dissolves the chlorides of potassium and sodium (formed by the action of the hydrochloric acid upon the silicates), and leaves the silica in white flakes. These may be collected upon a filter, and washed several times with distilled water. The

Fig. 199.—Air-gas blowpipe.

* If *tridymite*—a mineral which occurs in anhydrous hexagonal crystals, has a sp. gr. of 2.3, and is not attacked by alkalies—be regarded as the type of another crystalline variety of silica, this must be said to be *trimorphous*.

filter is then carefully spread out upon a hot iron plate, or upon a hot brick, and allowed to dry, when the silica is left as a dazzling white powder, which must be strongly heated in a porcelain or platinum crucible to expel the last traces of water. It is remarkable for its extreme lightness, especially when heated, the slightest current of air easily blowing it away.

169. For effecting such fusions as that just described, an air-gas blowpipe (Fig. 199) supplied with air from a double-action bellows, worked by a treadle, will be found most convenient.

170. *Silicates.*—The acid properties of silicic acid are so feeble that it is a matter of great difficulty to determine the proportion of any base which is required to react with it in order to form a chemically neutral salt. Like carbonic acid, it does not destroy the action of the alkalies upon test-papers, and we are therefore deprived of this method of ascertaining the proportion of alkali which neutralises it in a chemical sense. In attempting to ascertain the quantity of alkali with which silica combines, from that of the carbon dioxide which it expels when heated with an alkaline carbonate, it is found that the proportion of carbon dioxide expelled varies considerably, according to the temperature and the proportion of alkaline carbonate employed. The limits of the reaction however appear to be the formation of the alkali metasilicate on the one hand and the alkali orthosilicate on the other:

$$SiO_2 + Na_2CO_3 = CO_2 + Na_2SiO_3 \text{ (metasilicate)}$$
$$SiO_2 + 2Na_2CO_3 = CO_2 + Na_4SiO_4 \text{ (orthosilicate).}$$

By heating silica with sodium hydroxide (NaOH), it is found that 60 parts of silica expel 36 parts of water, however much NaOH is employed, and the same proportion of water is expelled from barium hydroxide, $Ba(OH)_2$, when heated with silica.

The formula SiO_2 represents 60 parts by weight of silica, and 36 parts represent two molecules of water. Hence it would appear that the action of silica upon sodium hydroxide is represented by the equation—$4NaOH + SiO_2 = Na_4SiO_4 + 2H_2O$; and that upon barium hydroxide by $2Ba(OH)_2 + SiO_2 = Ba_2SiO_4 + 2H_2O$: and since it is found that several of the crystallised mineral silicates contain a quantity of metal equivalent to H_4, it is usual to represent silicic acid as a *tetrabasic* acid, H_4SiO_4, containing 4 atoms of hydrogen exchangeable for metals.

The circumstance that silica is not capable of being converted into vapour at a high temperature, enables it to decompose the salts of many acids which, at ordinary temperatures, are able to displace silicic acid. The feebly acid character of SiO_2 will recall that of CO_2. Other comparison between these analogues is hardly possible on account of their different physical condition.

The silicates form by far the greatest number of minerals. The different varieties of clay consist of aluminium silicate; felspar is a silicate of aluminium and potassium; meerschaum is a silicate of magnesium.

The different kinds of glass are composed of silicates of potassium, sodium, calcium, lead, &c. None but the silicates of the alkali metals are appreciably soluble in water.

Scarcely any of the silicates are represented by formulæ which express their derivation from the acid H_4SiO_4; they are generally represented as derivatives of metasilicic acid and of *polysilicic* acids, *i.e.*, compounds of nH_2O with SiO_2 (compare p. 261).

This tendency of silicon to form complex mineral compounds is

comparable with that of its analogue, carbon, to form complex organic compounds, but whereas oxygen is the other element mostly concerned in the formation of mineral silicates, hydrogen is the predominant companion of carbon in organic derivatives.

171. **Silicon** or **silicium.**—From the remarkably unchangeable character of silica, it is not surprising that it was long regarded as an elementary substance. In 1813, however, Davy succeeded in decomposing it by the action of potassium, and in obtaining an impure specimen of silicon. It has since been produced, far more easily, by converting the silica into potassium silico-fluoride (K_2SiF_6), and decomposing this at a high temperature with potassium or sodium, which combines with the fluorine to form a salt capable of being dissolved out by water, leaving the silicon in the form of a brown powder (*amorphous silicon*), which resists the action of all acids, except hydrofluoric, which it decomposes, forming silicon fluoride, and evolving hydrogen ($Si + 4HF = SiF_4 + H_4$). It is also dissolved by solution of potash, with evolution of hydrogen, and formation of potassium silicate. It burns brilliantly when heated in oxygen, but not completely, for it becomes coated with silica which is fused by the intense heat of the combustion. When heated with the blowpipe on platinum foil, it eats a hole through the metal, with which it forms the fusible platinum silicide.

If potassium silico-fluoride be fused with aluminium, a portion of the latter combines with the fluorine, and the remainder combines with the silicon, forming aluminium silicide. By boiling this with hydrochloric and hydrofluoric acids in succession, the aluminium is extracted, and crystalline scales of silicon, with a metallic lustre resembling black lead, are left (*graphitoid silicon*). In this form the silicon has a specific gravity of about 2.5, and refuses to burn in oxygen, or to dissolve in hydrofluoric acid. A mixture of nitric and hydrofluoric acids, however, dissolves it. It burns spontaneously in fluorine, and when heated in chlorine. Like graphite, this variety of silicon conducts electricity, though amorphous silicon is a non-conductor. The amorphous silicon becomes converted into this incombustible and insoluble form under the action of intense heat. It is worthy of remark that the combustibility of amorphous carbon (charcoal) is also very much diminished by exposure to a high temperature.

Unlike carbon, however, silicon is fusible at a temperature somewhat above the melting-point of cast-iron; on cooling, it forms a brilliant metallic-looking mass, which may be obtained, by certain processes, crystallised in octahedra so hard as to scratch glass like a diamond.

In their chemical relations to other substances there is much resemblance between silicon and carbon. Silicon, however, is capable of displacing carbon, for if potassium carbonate be fused with silicon, the latter is dissolved, forming potassium silicate, and carbon is separated. Silicon also resembles carbon in its disposition to unite with certain metals to form compounds which still retain their metallic appearance. Thus silicon is found together with carbon in cast-iron, and it unites directly with aluminium, zinc, and platinum, to form compounds resembling metallic alloys. Nitrogen enters into direct union with silicon at a high temperature, though it refuses to unite with carbon except in the presence of alkalies.

The most important analogy between carbon and silicon from a theoretical point of view, resides in the fact that each of them combines with hydrogen in the proportion of one atom of the element to four atoms of hydrogen, showing that each is a tetravalent element.

Silicon carbide, SiC.—As might be expected from their similarity, carbon and silicon do not combine easily. At the temperature of the electric furnace (3500° C.), however, the compound SiC is produced in the form of colourless, transparent hexagonal plates of sp. gr. 3.12. It is hard enough to scratch the ruby, and on this account is made on a considerable scale for use as an abrasive material under the name *carborundum* which is generally dark coloured from impurities. It resists the attack of all acids, but succumbs to fused alkali; it does not oxidise even at a white heat.

In the manufacture of carborundum the electric furnace consists of a brick box, having a carbon electrode projecting into each end. The bottom of the box having been covered up to the level of the electrodes with a mixture of sand, coke, and a little salt, a layer of crushed coke of the same cross-section as the electrodes is built up between the electrodes. The furnace is then filled with the aforesaid mixture. When the electric current is supplied to the electrodes the layer of coke between them attains a very high temperature owing to the resistance it offers to the passage of the current, and the radiation from this hot core causes the carbon in the charge to reduce the silica and to combine with the silicon for a certain distance around the core; $SiO_2 + C_3 = SiC + 2CO$.

Silicon nitride, SiN (?), has been obtained by heating silica with carbon in a blast furnace and treating the product successively with hydrofluoric acid and potash, when the nitride is left as a green infusible powder which is attacked by potash at a red heat, yielding potassium silicate, hydrogen, and ammonia. Si_3N_3 is formed by heating silicon in nitrogen.

Silicon hydride, SiH_4, is the analogue of marsh gas, CH_4, but is much less stable. It is prepared by decomposing magnesium silicide Mg_2Si (made by heating magnesium with silica) with dilute HCl. It is a colourless gas which, unlike CH_4, ignites spontaneously in air, burning with a brilliant white flame which emits clouds of silica and deposits a brown film of silicon upon a cold surface. Pure SiH_4 does not appear to be spontaneously inflammable, resembling pure PH_3 in this respect, and also in the influence which pressure has upon its spontaneous explosion when mixed with oxygen.

Silico-acetylene, Si_2H_2, is produced when *calcium silicide*, $CaSi_2$ the analogue of calcium carbide (p. 137), is treated with dilute acid; $CaSi_2 + 2HCl = CaCl_2 + Si_2H_2$. The silicide is made by heating a mixture of lime, silica, and carbon in the electric furnace, and the silico-acetylene is a yellow crystalline substance.

When cast-iron containing silicon is boiled with hydrochloric acid until the whole of the iron is dissolved, a grey frothy residue is left. If this be collected on a filter, well washed and dried, it is found to consist of black scales of graphite, mixed with a very light white powder. On boiling it with potash, hydrogen is evolved and the white powder dissolves, forming a solution containing potassium silicate. This white powder appears to be identical with a substance obtained by other processes, and called *leucone*,* which is believed to have the composition $Si_2H_2O_3$ or $O(SiOH)_2$. Its action upon solution of potash would be explained by the equation—

$$Si_2H_2O_3 + 4KOH = 2K_2SiO_3 + H_2O + H_4$$

Leucone is slowly converted into silicic acid, even by the action of water, hydrogen being disengaged. It burns when heated in air.

Other compounds of this character have been prepared.

172. Silicon tetrachloride, $SiCl_4$, unlike the chlorides of carbon, may be formed by the direct union of silicon with chlorine at a high temperature; but it is best prepared by passing dry chlorine over a mixture of silica and charcoal, heated to redness in a porcelain tube connected with

* Λευκὸς, white.

a receiver kept cool by a freezing-mixture. Neither C nor Cl separately attacks the silica, but when they are employed together, the combined attractions of the carbon for the oxygen and the chlorine for the silicon decomposes the silica; $SiO_2 + C_2 + Cl_4 = SiCl_4 + 2CO$.

The tetrachloride is a colourless heavy liquid (sp. gr. 1.52), which is volatile (boiling-point, 59° C.), and fumes when exposed to air, the moisture of which decomposes it yielding hydrochloric acid and silicic acid; $SiCl_4 + 4HOH = Si(OH)_4 + 4HCl$.

When silicon is heated in hydrogen chloride a compound, which, from its analogy with chloroform, $CHCl_3$, is termed *silico-chloroform*, $SiHCl_3$, is obtained; $Si + 3HCl = SiHCl_3 + H_2$. This is a colourless liquid which boils at 36° C., and, unlike most chlorine compounds (including chloroform), is inflammable, burning with a greenish flame, and producing SiO_2 and HCl.

The chlorides of silicon have not received any practical application on a large scale, but they are of theoretical importance as forming the starting-point of a number of silicon compounds which are the analogues of organic carbon compounds, C being exchanged for Si.

Silicon hexachloride, $Cl_3Si - SiCl_3$, is produced when $SiCl_4$ is passed over fused silicon at a very high temperature. It forms colourless crystals melting at −1° C. and boiling at 147° C. Cold water decomposes it with formation of *silico-oxalic acid*, $Cl_3Si \cdot SiCl_3 + 4HOH = HOOSi \cdot SiOOH + 6HCl$.

Silicon tetrabromide, $SiBr_4$, is a colourless liquid of sp. gr. 2.82, b.p. 150° C. and m.p. −12° C. *Silicon tetraiodide*, SiI_4, crystallises in colourless octahedra, melts at 120° C., and boils at 290° C.

173. **Silicon tetrafluoride** ($SiF_4 = 104$ parts by weight).—If a mixture of powdered fluor spar and glass be heated, in a test-tube or small flask, with concentrated sulphuric acid, a gas is evolved which has a very pungent odour, and produces thick white fumes in contact with the air:* it might at first be mistaken for hydrofluoric acid, but a glass rod or tube moistened with water and exposed to the gas, becomes coated with a white film, which proves, on examination, to be silica. This result originated the belief that the gas consisted of fluoric (now hydrofluoric) acid and silica; but Davy corrected this view by showing that it really contained no oxygen, and consisted solely of silicon and fluorine. The gas is now called silicon tetrafluoride, and represents silica in which the oxygen has been displaced by fluorine: the change of places between these two elements in the above experiment is represented by the equation—

$$2CaF_2 + SiO_2 + 2H_2SO_4 = 2CaSO_4 + SiF_4 + 2H_2O.$$

The formation of the crust of silica upon the wetted surface of the glass is due to a reaction between the tetrafluoride and the water, in which the oxygen and fluorine again change places; $SiF_4 + 2H_2O = SiO_2 + 4HF$.† Since this latter equation shows that hydrofluoric acid is again formed, it would be expected that the glass beneath the deposit

* SiF_4 becomes solid at −102° C., and, at a higher temperature, evaporates without fusing.

† It will be noticed that the proportion of SiF_4 to H_2O in this equation, representing the decomposition of the gas by water, is the same as that in the preceding equation, representing the evolution of the gas together with water, so that the equations seem to contradict each other. In reality it depends on the actual masses of water and other substances present, and also on the temperature, whether SiF_4 and H_2O can exist together or will at once decompose each other. The excess of sulphuric acid used in the manufacture of SiF_4 will combine with the water, and will prevent it from decomposing the SiF_4.

of silica would be found corroded by the acid; this, however, is not the case, and when the experiment is repeated upon a somewhat larger scale, so that the water which has attacked the gas may be examined, it is found to hold in solution, not hydrofluoric acid, but an acid which has little action upon glass, and is composed of hydrofluoric acid and silicon fluoride, the hydrofluoric acid produced when water acts on the fluoride having combined with a portion of the latter to produce the new acid, $2HF.SiF_4$, or H_2SiF_6, *hydrofluosilicic acid.*

For the preparation of silicon tetrafluoride, 30 grams of fluor spar and an equal weight of powdered glass are mixed together, and heated in a Florence flask, with 200 c.c. of oil of vitriol, the gas being collected in dry bottles by downward displacement (see Fig. 150, p. 177). If a little of the gas be poured from one of the bottles into a flask filled up to the neck with water, the surface of the latter will become covered with a layer of silica, so that if the flask be quickly inverted, the water will not pour from it, and will seem to have been frozen. In a similar manner, a small tube filled with water and lowered into a bottle of the gas, will appear to have been frozen when withdrawn. A stalactite of silica some inches in length may be obtained by allowing water to drip gently from a pointed tube into a bottle of the gas. Characters written on glass with a wet brush are rendered opaque by pouring some of the gas upon them.

The fact that silica is so easily volatilised in the form of SiF_4 is of immense service in analytical chemistry for "opening up" mineral silicates. By heating the silicate with H_2SO_4 and HF in a platinum vessel all the silica may be expelled, leaving the bases in the form of sulphates.

174. **Hydrofluosilicic acid** ($H_2SiF_6 = 144$ parts by weight).—This acid is obtained in solution by passing silicon tetrafluoride into water; $3SiF_4 + 2H_2O = 2H_2SiF_6 + SiO_2$.

The gas must not be passed directly into the water, lest the separated silica should stop the orifice of the tube, to prevent which the latter should dip into a little mercury at the bottom of the water, when each bubble, as it rises through the mercury into the water, will become surrounded with an envelope of gelatinous silica, and if the bubbles be very regular, they may even form tubes of silica extending through the whole height of the water.

Crystals of $H_2SiF_6.2Aq$ have been obtained by passing SiF_4 into solution of HF.

Fig. 200.—Preparation of hydrofluosilicic acid.

For preparing hydrofluosilicic acid, it will be found convenient to employ a gallon stoneware bottle (Fig. 200), furnished with a wide tube dipping into a cup of mercury placed at the bottom of the water. 500 grams of finely powdered fluor spar, an equal weight of fine sand, and 2 litres of oil of vitriol are introduced into the bottle, which is gently heated upon a sand-bath, the gas being passed into about 3 litres of water. After six or seven hours the water will have become pasty, from the separation of gelatinous silica. It is poured upon a filter, and when the liquid has drained through as far as possible, the filter is wrung in a cloth, to extract the remainder of the acid solution, which will have a sp. gr. of about 1.078.

A dilute solution of hydrofluosilicic acid may be concentrated by evaporation up to a certain point, when it begins to decompose, evolving fumes of SiF_4, HF remaining in solution and volatilising in its turn if the heat be continued. Of course, the solution corrodes glass and porcelain when evaporated in them. If the solution of hydofluosilicic acid be neutralised with potash, and stirred, a very characteristic crystalline precipitate of *potassium silico-fluoride* (potassium fluosilicate), K_2SiF_6, is formed; $H_2SiF_6 + 2KHO = K_2SiF_6 + 2H_2O$.

But if an excess of potash be employed, a precipitate of gelatinous silica will be separated, potassium fluoride remaining in the solution—

$$H_2SiF_6 + 6KHO = 6KF + 4H_2O + SiO_2.$$

One of the chief uses of hydrofluosilicic acid is to separate the potassium from its combination with certain acids, in order to obtain these in the separate state.

Tin and lead, which belong to the same group of elements as silicon (*see* "Periodic Law"), form *fluostannates* and *fluoplumbates*, such as Na_2SnF_6 or $2NaF.SnF_4$, and K_2PbF_6 or $2KF.PbF_4$, analogous to the fluosilicates.

175. *Silicon disulphide* (SiS_2), corresponding with carbon disulphide, is obtained by burning silicon in sulphur vapour, or by passing vapour of carbon disulphide over a mixture of silica and charcoal, in the form of volatile needles. Unlike the carbon compound, it is a white amorphous solid, absorbing moisture when exposed to air, and soluble in water, which gradually decomposes it into silica and hydrogen sulphide. When heated in air it burns slowly, yielding silica and sulphur dioxide.

176. The elements carbon, boron, and silicon possess many properties in common. They all exist in the amorphous and the crystalline forms; all are incapable of being converted into vapour; all exhibit a want of disposition to dissolve; all form feeble acid oxides by direct union with oxygen, for which the order of their affinity is boron, silicon, carbon; and all unite with several of the metals to form compounds which resemble each other. Boron and silicon are capable of direct union with nitrogen, and so is carbon if an alkali be present. Recent researches attribute to silicon the power of occupying the place of carbon in some organic compounds, and the formula of leucone, $Si_3H_2O_3$ strongly reminds us of the organic compounds of carbon with hydrogen and oxygen. In many of its physical and chemical characters silicon is closely allied with the metals, and it will be found that tin and titanium bear a particular resemblance to it in their chemical relations.

Notwithstanding these points of similarity between boron, carbon, and silicon, boron is not regarded as belonging to the family of elements which includes carbon and silicon, because whilst C and Si are tetravalent elements, boron is trivalent, and must, therefore, be classed with nitrogen and phosphorus.

CERTAIN GENERAL PRINCIPLES.

Atoms and Molecules.

177. It is only after numerous facts have been observed, and accurately described, that it is possible to deduce such general principles as may enable future workers to conduct their experiments in such a manner that they may discover and arrange fresh facts with the smallest possible expenditure of energy and time. Thus, the generalisation which receives the name of the *Atomic Theory*, and upon which the science of Chemistry is now constructed, was enunciated at the beginning of the last century only after the gravimetric and volumetric composition of a large number of compounds had been determined by both synthetical and analytical methods.

The theory arose from the contemplation of the quantitative composition of various compounds, when it was seen that chemical combination does not occur between masses of matter in indefinite quantities, but is controlled by the following three laws:

(1) *Law of Constant Proportions.*—In every compound the masses of the constituent elements bear the same ratio to each other, from whatever source the compound may be obtained.

It is this law which determines how much of an element in a mixture will enter into combination. For example, when a mixture of zinc and sulphur is heated, complete combination will only occur when the ratio of the mass of zinc to that of sulphur is 65·5 : 32; if the mixture contain the elements in any other ratio, either zinc or sulphur will remain uncombined after the heating.

(2) *Law of Multiple Proportions.*—When two elements combine to form more than one compound, the masses of the one element combining with a constant mass of the other, must be simple multiples of the smallest mass among them.

The hydrocarbons yield abundant examples of this law; thus, quantitative analysis of marsh gas, olefiant gas, and acetylene shows that they have the following gravimetric compositions per cent.:

	Carbon.	Hydrogen.	Ratio of C : H.
Marsh gas	75	25	3 : 1
Olefiant gas	85.7	14.3	6 : 1
Acetylene	92.3	7.7	12 : 1

It is apparent from the ratios that the proportion of carbon that combines with one part by weight of hydrogen in the second and third compounds, is a multiple of that in the first compound by a simple whole number.

Another striking example is afforded by the oxides of nitrogen; in these there are, for 100 parts of nitrogen, 57.1, 114.2, 171.3, 228.4 and 285.5 parts of oxygen respectively, figures in the ratio 1:2:3:4:5.

(3) *Law of Reciprocal Proportions.*—When an element forms a compound with each of several other elements, the masses of the several other elements which combine with a constant mass of the first element, are also the masses of these elements which combine with each other, or they bear some simple ratio to these masses.

Thus, sulphuretted hydrogen, sulphur dioxide, and carbon bisulphide have the following gravimetric compositions:

	Per cent.		Per cent.
Sulphuretted hydrogen .	Sulphur 94.1 . .	Hydrogen	5.9
Sulphur dioxide . .	Sulphur 50.0 . .	Oxygen	50.0
Carbon bisulphide . .	Sulphur 84.2 . .	Carbon	15.8

When these figures are calculated for 100 parts of sulphur in each case, they become—

Sulphuretted hydrogen .	Sulphur 100 . .	Hydrogen	6.2
Sulphur dioxide . .	Sulphur 100 . .	Oxygen	100
Carbon bisulphide . .	Sulphur 100 . .	Carbon	18.7

The ratios of the proportions of C, H and O which combine with 100 parts of sulphur in the above table are:—

C : H	=	18.7 :	6.2	or	3 : 1
C : O	=	18.7 :	100	or	3 : 16
H : O	=	6.2 :	100	or	1 : 16

Now 3 compounds of carbon with hydrogen, 2 of carbon with oxygen, and 2 of hydrogen with oxygen are known, and the ratios of the elements in these compounds are:

C : H	=	3 : 1	6 : 1	12 : 1
C : O	=	3 : 8	3 : 16	
H : O	=	1 : 8	1 : 16	

Thus the ratio in which any pair of these elements combine with each other is either the same as that in which they combine with a constant mass of sulphur or is some multiple or submultiple thereof by a simple whole number.

In order to account for the existence of these laws, Dalton revived the atomic theory. The fundamental conception on which this theory is based has been stated in the Introduction; the new significance with which Dalton invested it was, that *each of the indivisible particles (atoms) of which a kind of matter is composed has an invariable weight, and that this weight is the same for each atom of the same kind of matter.* Furthermore, when combination of one kind of matter with another occurs, the union takes place between the atoms of these kinds of matter, and consists in the addition of one or more atoms of the first kind to one or more atoms of the second kind. If these postulates be granted, it at once becomes apparent why a compound always contains its elements in the same gravimetric ratio; water, for instance, is always composed of oxygen and hydrogen in the ratio of 8 : 1 by weight; and this, according to Dalton, is due to the fact that water is a compound of one atom of oxygen with one atom of hydrogen, the atom of oxygen weighing 8 times as much as the atom of hydrogen. The "atom" of

water, as Dalton called it, should therefore be represented as HO. The considerations which led to the adoption of H_2O for the formula of water will be dealt with presently.

Again, the law of multiple proportions follows of necessity from Dalton's hypothesis. For if a compound of x atoms of one element with y atoms of another element exist, a new compound can only be formed by adding another atom or by taking one away; and since each atom of the same element weighs the same, the addition or subtraction of each atom must cause the same variation in the proportional composition. Thus, if there be a compound of one atom of nitrogen with one atom of oxygen, and the ratio between the weights of these atoms be 7 : 8 (or 100 : 114.2), it is only possible to produce another compound of these two elements by adding one or more atoms of nitrogen, each weighing 7, or one or more atoms of oxygen, each weighing 8; so that any other oxide of nitrogen must contain the elements in the ratio $7 \times n : 8 \times m$ by weight, n and m being integers.

The third law of chemical combination is equally explicable, for the ratio by weight in which two elements combine is either the ratio between the weights of their atoms, or that between some multiples of these. Hence the ratio between the weights of two elements in a compound must be represented by the same numbers as those representing the weights of these elements in their compounds with any other elements, or by some simple multiple or submultiple of these weights. If the compound of carbon with sulphur which contains these elements in the proportion of 18.7 : 100 or 3 : 16 parts by weight, contain only one atom of sulphur and one atom of carbon, then any compound of sulphur with another element, itself capable of combining with carbon in the proportion of x : 3, must contain the sulphur and the other element in the proportion of $16 : x$ or $16 \times n : x$, where n is an integer; if, on the other hand, the compound of carbon with sulphur contain 2 or 4 atoms of sulphur, other compounds of this element may contain it in the proportion of 8 or 4 parts by weight.

Dalton endeavoured to construct a table of atomic weights—that is, a table of the relative weights of the atoms—by determining how many parts by weight of each element combine with one part by weight of hydrogen, the atomic weight of which he took as unity, hydrogen being the lightest kind of matter. His numbers, however, agree only in a few cases with the modern atomic weights, for two reasons. In the first place, except in those cases in which two elements form more than one compound—the difference between which compounds he attributed to their containing different numbers of atoms—except in these cases, he concluded that combination occurs between one atom and one atom, whereas now the hypothesis is that in many cases the combination is between 2 or 3 atoms and 1 atom, or, generally, between n and m atoms. For instance, if the compound of carbon and hydrogen in which the ratio by weight of C : H is 3 : 1 be a compound of 1 atom of C with 1 atom of H the atomic weight of carbon will be 3; if, as now believed, it is a compound of 1 atom of C with 4 atoms of H, the atomic weight of carbon is 12.

In the second place, Dalton had not conceived the existence of a second kind of ultimate particle, now called a *molecule*. Thus, he spoke of an "atom" of water and other compounds, notwithstanding that by his hypothesis an atom is indivisible, while by definition a compound is divisible. His studies of gases were limited to their combination by weight. Gay-Lussac (1809) studied their combination by volume, and experienced a difficulty in applying Dalton's hypothesis, which led to the conception of molecules.

The difficulty is easily appreciated from the contemplation of the combination of hydrogen with chlorine. Equal volumes of these gases

combine, and the product occupies twice the volume of either of its constituents: one volume of H combines with one volume of Cl to form two volumes of HCl. According to Dalton's theory, one atom of hydrogen combines with one atom of chlorine to form one "atom" of hydrogen chloride. If this be the case, *equal volumes of hydrogen and chlorine must contain the same number of atoms*, for it is found that equal volumes of these gases combine exactly—that is, no residue of either gas is left. This reasoning applies to the combination of several other gases, whence Gay-Lussac attempted to deduce the generalisation that equal volumes of all gases contain the same number of atoms. But if this be the case, the two volumes of HCl, produced by the combination of one volume of H with one volume of Cl, must contain twice as many atoms as the one volume of chlorine or of hydrogen contains; therefore one atom of Cl combines with one atom of H to form two atoms of HCl, and consequently one atom of HCl must contain half an atom of Cl, which is impossible, an atom being indivisible. Gay-Lussac's generalisation, however, corrected some of Dalton's atomic weights to the present values; that of oxygen will serve as an example. Two volumes of H combine with one volume of O to form water; but equal volumes of gases contain the same number of atoms, therefore 2 atoms of H combine with one atom of O; the ratio by weight of H to O in water is, however, 1 : 8, so that 2 atoms of H weighing 1 combine with 1 atom of O weighing 8; but, as already defined, 1 atom of hydrogen is to weigh 1, therefore water contains 2 atoms of hydrogen weighing 2, combined with one atom of oxygen weighing 16, and its formula is H_2O.

Avogadro (1811) conceived the existence of two kinds of ultimate particle. Starting with the conception that gases are composed of ultimate particles, which he preferred to call *molecules*, he attempted to explain the combination of gases by volume, but encountered the difficulty experienced by Gay-Lussac. To overcome this difficulty he had recourse to the supposition that the molecules of the gases are shattered before combination occurs, and that the parts of the molecules then recombine to form the molecules of the new gas. The particles produced by the scission of the molecules were the true indivisibles, or Dalton's atoms. Thus, Avogadro was able to support the generalisation now known as *Avogadro's Law*, namely, that *equal volumes of gases at the same temperature and pressure contain the same number of molecules*. The combination of hydrogen with chlorine is now easily explained; one volume of hydrogen contains the same number of molecules as is contained in one volume of chlorine; when these volumes combine, the molecules are shattered and their component atoms recombine to form molecules of hydrogen chloride; one molecule of chlorine thus reacts with one molecule of hydrogen to form two molecules of hydrogen chloride, which (according to Avogadro's law) must therefore occupy twice the volume occupied by either the chlorine or the hydrogen.

The definitions of an atom and of a molecule have been given on p. 8. The hypothesis that the hydrogen molecule consists of two atoms may be supported as follows: Hydrogen chloride contains half its volume of hydrogen, and therefore half as much hydrogen as is contained in an equal volume of hydrogen; but equal volumes of hydrogen chloride and hydrogen contain the same number of molecules (Avogadro's law),

therefore one molecule of hydrogen chloride contains half as much hydrogen as one molecule of hydrogen contains. Now one molecule of hydrogen chloride is supposed to consist of one atom of hydrogen combined with one atom of chlorine, therefore one molecule of hydrogen must be supposed to consist of one atom of hydrogen combined with one atom of hydrogen. The same reasoning will apply to the molecule of chlorine.

It is difficult to account for the spontaneous intermixture or *diffusion* of gases (p. 25) unless it be granted that their molecules are always in motion, and if this be postulated an explanation of the pressure of a gas is at once found. For if the molecules are in constant motion they must continually strike the sides of the containing vessel and the numerous impacts must exert a pressure on those sides.

Liquids also have the property of diffusion, but the property is not universal between all liquids; thus, oil and water do not intermix. Moreover, the diffusion occupies a much longer time than that of gases. It seems therefore that molecular motion must also exist in liquids, but at a slower rate or more limited than that in gases. Diffusion among solids is rare though not unknown (p. 25), but the process is so exceedingly slow that molecular motion of solids must be more limited than that of liquids.

Now by heating a gas its pressure is increased, and if the pressure is due to the motion of the molecules, it follows that increase of the temperature of the gas means increase of molecular motion. Conversely, cooling a gas decreases its pressure, and therefore also its molecular motion. All gases save hydrogen (which requires pressure) can be liquefied by merely cooling them, that is, by depriving their molecules of motion to a sufficient extent.

The movement of the molecules of a solid may be regarded as limited to a species of oscillation, that is to say, the molecules cannot move far from their original positions. As this movement is increased by rise of temperature there is a tendency for the molecules to move so fast that they break away from the influence of each other, and are imbued with much more freedom of motion. The temperature at which this happens is the melting-point of the solid, and is constant until the whole mass is liquid, since heat is absorbed in order to effect the work of separating the molecules.

The molecules of a liquid are still considerably under the influence of each other, although those at the surface escape and move about in the space above the liquid without influencing each other to any but a very limited extent; this is the evaporation of the liquid. When the space is confined, it soon becomes saturated with these vapour molecules, and evaporation apparently ceases. This happens when as many molecules of vapour attach themselves to the surface of the liquid as escape from it, in unit time.

As the temperature of the vapour is raised, the motion of the molecules becomes more rapid, and the latter are less and less influenced by each other. The vapour is then a gas, and conforms with the laws which connect the volume of a gas with its pressure and temperature (see p. 27).

If an ideal gas (see p. 28) consists of a number of elastic solid particles in motion, its properties can be investigated by mathematics; this

has been done, and the results are generally spoken of as the *kinetic theory** of gases, which may be succinctly stated thus: The molecules of a gas are in constant and rapid motion in straight lines, and continue moving in the same direction until they are reflected by striking each other or the walls of the containing vessel. The impacts against the sides of the vessel give rise to the pressure of the gas, whilst the temperature of the gas is a measure of the velocity of motion of the molecules.

The theory is not strictly within the province of the chemist, but in that of the physicist; the former, however, finds in it an explanation of many chemical changes, and, above all, a confirmation of Avogadro's hypothesis, originally deduced from purely chemical considerations, that equal volumes of gases at the same temperature and pressure contain the same number of molecules. Moreover, the theory teaches him that the hypothesis is absolutely true only of perfect gases.

A mathematical expression for the pressure of a gas may be deduced from consideration of molecules moving in a hollow cube. Let a molecule of mass m in such a vessel be moving in any direction with velocity w; this can be resolved into three components (x, y, z) in directions parallel to the sides of the cube and according to the principle of the resolution of velocities, $w^2 = x^2 + y^2 + z^2$. When the molecule moving towards the side of the cube with velocity x strikes the side, it exerts a force equivalent to its momentum, which is mx, not only at the impact but when it rebounds, making a total of $2mx$. If l is the distance that the molecule has to move from one side of the cube to the other, that is, the length of the side of the cube, this force is repeated x/l times every unit of time. Thus the force exerted in unit time becomes $2mx \times x/l = 2mx^2/l$. What is true of component x applies to the other components, so the expression becomes $2m(x^2 + y^2 + z^2)/l = 2mw^2/l$, and for the whole number n of the molecules, $2nmw^2/l$. The pressure p of a gas is expressed per unit area, so the foregoing expression must be divided by $6l^2$, the number of units of surface in a cube; hence the final formula is $p = \frac{2nmw^2}{6l^3}$. l^3 is the volume (v) of the cube, so the expression may be written $pv = \frac{nmw^2}{3}$, or for unit volume $p = \frac{nmw^2}{3}$.

It is more instructive to write this formula $p = \frac{2}{3} n \frac{mw^2}{2}$, for $\frac{mw^2}{2}$ is the kinetic energy of the moving molecule and $nmw^2/2$ that of all the molecules. Now if p is varied by altering the temperature of the gas, this variation can be due only to the variation of the kinetic energy of the molecules for n is constant. Hence the temperature of a gas must be a measure of its kinetic energy, and if unit volumes of two gases have the same temperature they must also have the same kinetic energy, or $mw^2/2 = m_1 w_1^2/2$. Let the unit volumes be also at the same pressure, then $\frac{2}{3} n \frac{mw^2}{2} = \frac{2}{3} n_1 \frac{m_1 w_1^2}{2}$ or $mnw^2 = m_1 n_1 w_1^2$, or since $mw^2 = m_1 w_1^2$ by the previous equation, $n = n_1$, that is to say, when gases are at the same temperature and pressure the number of molecules in unit volume is the same (Avogadro's hypothesis).

The mass of a volume of gas must be the product of the mass of each molecule and the number of molecules; hence mn in the foregoing equations is the mass of the gas. Taking 1 gram of hydrogen which measures 11,110 c.c. at 760 mm. pressure and 0° C., mn will be 1, and we have $pv = w^2/3$ or $w = \sqrt{3pv}$. The pressure of 760 mm. of mercury in absolute units of mass is $76 \times 13.5 \times g = 1013130$. Hence the rate w at which the hydrogen molecules move is— $\sqrt{3} \times 1013130 \times 11110$ cm. per second, or 1838 metres per second.

The mass of unit volume is identical with density, hence for mn in the foregoing equations might be written d, and it will be obvious that if p and v are constant w must vary inversely as $\sqrt{d}$. That is to say, the velocity of the molecules of a gas

* κινησις = motion.

varies inversely as the square root of the density of the gas. Since in equal volumes of two gases at the same temperature and pressure $mnw^2 = m_1 n_1 w_1^2$ it follows that $dw^2 = d_1 w_1^2$; that is to say, the rates of movement of the molecules of different gases vary inversely as the square roots of their specific gravities.

Molecular Weights.—The weight of a single molecule has never been determined, and it is assumed that all the molecules of any single substance have the same weight. To compare the weights of the molecules of different substances is possible if Avogadro's hypothesis be true. For if equal volumes of gases at the same temperature and pressure contain the same number of molecules, the relative weights of these volumes must also be the relative weights of the molecules of the gases. The molecule of hydrogen being selected as the standard of comparison, the unit of molecular weights is 2, since it is accepted that there are two parts or atoms in each molecule of hydrogen, and the molecular weight of any other gas, be it element or compound, is *twice the number of times that a volume of it in the state of gas is heavier than an equal volume of hydrogen* at the same temperature and pressure. This is expressed by the equation $M = 2D$, where M is the molecular weight, and D the vapour density * of the gas, for the latter is the number of times that the gas is heavier than hydrogen.

Hence, in order to ascertain the molecular weight of a substance it is necessary to determine the vapour density and to double this value. When the substance is a gas at the ordinary temperature, the operation consists in weighing a volume of the gas; this weight is then divided by that of the same volume of hydrogen at the same temperature and pressure, calculated on the basis of the ascertained weight of one litre of hydrogen at 0°C. and 760 mm. pressure, namely 0.09 gram.

In the actual process, the capacity (about 500 c.c.) of a globe (closed by a stop-cock such as that shown in Fig. 50) is determined by weighing it, first empty, and then full of water; the weight of the water which it can contain, and, therefore, its volume (1 c.c. of water weighs 1 gram at 4°C.) is thus ascertained. The dried globe may then be filled with the purified gas, the temperature and pressure being noted at the moment when the stop-cock is closed, and again weighed.

Let the weight of the empty globe be w grams, and that of the globe full of water at 4° C. be W grams; then the capacity (V) of the globe is $W - w$ c.c. Let W_1 be the weight of the globe filled with carbon dioxide (CO_2) at 15° C. and 770 mm. bar. Then $W_1 - w$ grams is the weight of V c.c. of CO_2 at 15° and 770 mm. bar. Since the volume of a gas varies inversely as its pressure, and directly with its absolute temperature (degrees C + 273), V c.c. of *hydrogen* at 15° C. and 770 mm. bar. will be $V \times \frac{770}{760} \times \frac{273}{285}$ c.c. at 0° C. and 760 mm., and will weigh $V \times \frac{770}{760} \times \frac{273}{285} \times 0.0009 = A$ grams.

Thus $\frac{W_1 - w}{A}$ = vapour density of CO_2, and $\frac{2(W_1 - w)}{A}$ is the molecular weight of CO_2.

When the substance has to be heated to convert it into a gas, the same method may be adopted, the solid or liquid substance being introduced into the globe, which is then heated in a bath of liquid at a sufficiently high temperature to volatilise the substance entirely; the vapour,

* The term vapour density is used here because so few substances being gaseous at the ordinary temperature, it is nearly always necessary to vaporise the substance before it can be regarded as a gas.

in escaping from the globe, expels the air, and when no more vapour issues from the narrow orifice of the neck (which is substituted for the stop-cock), a blowpipe flame is applied to seal this orifice, the temperature of the bath and the pressure of the atmosphere being noted at the moment of sealing. The calculations involved are the same as those stated above. For substances which volatilise at temperatures above that at which glass becomes soft, globes made of porcelain must be employed; these are sealed by the oxyhydrogen blowpipe. When modified in this way for solids and liquids, the method is known as *Dumas' method.*

The foregoing method for determining vapour densities consists in weighing a known volume of vapour. The value can be equally well, and somewhat more easily, ascertained by measuring the volume occupied by a known weight of vapour, an operation which is most easily effected by the *Victor Meyer method.* In this, a weighed quantity of the substance is converted into vapour in a vessel containing air (or some other gas), and the volume of air displaced by the vapour is collected and measured.

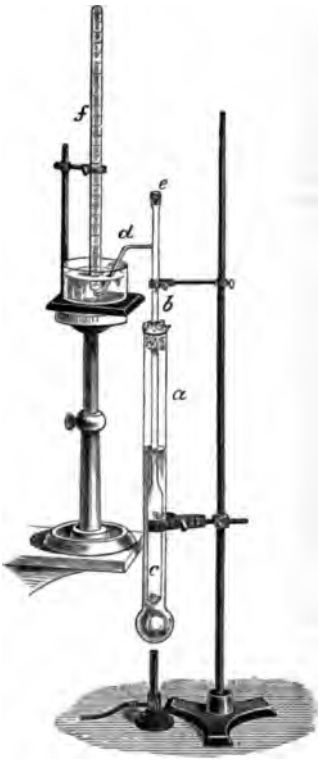


Fig. 201.—Victor Meyer's apparatus.

Take, for example, the determination of the vapour density of alcohol, which boils at 78.3° C. The vapourising tube (*b*, Fig. 201), well closed by a cork, is heated in the cylinder of boiling water *a* so long as any bubbles of air pass from the opening of the delivery-tube *d* through the water in the trough. The end of the delivery-tube is then inserted into the graduated tube *f*, which is full of water. About 0.1 gram of alcohol is weighed out into a small tube, which is dropped into the opening of the vapourising-tube, this being then quickly corked. A little asbestos is placed at the bottom of the vapourising-tube *c* to prevent breakage.

The alcohol vapour expels a volume of air equal to its own, and this is collected in the tube *f*, and accurately measured, with the usual corrections for temperature and pressure. The volume of a known weight of alcohol in the form of vapour having been thus ascertained, the vapour density may be calculated.

For example, 0.1 gram of alcohol expelled a volume of air which measured 48.5 c.c. when corrected to 0° C. and 760 mm. bar. Hence, supposing that alcohol could retain the state of vapour at that temperature and pressure, 48.5 c.c. of alcohol vapour would weigh 0.1 gram.

Now, 48.5 c.c. of hydrogen at 0° C. and 760 mm. weighs 0.00434 gram. so that the vapour density of alcohol is $\frac{0.1}{0.00434} = 23$, and its molecular weight is $23 \times 2 = 46$.

For substances which can only be volatilised at very high temperatures porcelain must be substituted for glass, and a liquid of high boiling-point must be used in the bath surrounding the vapourising tube.

It will be obvious that the molecular weight of a compound which is not capable of being vapourised without decomposition cannot be ascertained from the vapour density. There are, however, other criteria, by means of which the molecular weight of a compound may be ascertained; these will receive notice presently.

Inasmuch as Avogadro's law is true only of the ideal gas, the foregoing method of determining molecular weights can give accurate results only with gases which are far removed in temperature from the boiling-point of the corresponding liquids, and thus approach perfection. A criterion for the degree of gaseous character is the amount by which a gas deviates from Boyle's law; if, for instance, on doubling the pressure on 1000 c.c. the volumes becomes 400 c.c. instead of 500 c.c., the gas is far removed from perfection.

Another criterion is the behaviour of the gas when heated; if 1000 c.c. at 0° C. (273° absolute) expand to 2100 c.c. instead of 2000 c.c. when heated to 273° C. (546° absolute), the molecules of the gas must have been considerably under the influence of each other at the lower temperature, for the volume of a true gas must vary proportionally to the absolute temperature. If on heating the gas in question beyond 273° C. its volume increases in direct proportion to the absolute temperature, it may be concluded that at these higher temperatures the gas is nearly a true gas.

Now hydrogen, the standard for vapour densities, expands like a true gas, so that if the vapour density* of a gas which expands more rapidly than a true gas (hydrogen) is determined at different temperatures it is found not to be constant, but to grow less as the temperature rises. For example, at 273° C., 1000 c.c. of hydrogen contain 1/2 the matter contained in 1000 c.c. at 0° C., whereas in 1000 c.c. of the gas cited above (as expanding to 2100 c.c. at 273° C.) there is at 273° C. only 1/2.1 the matter that is contained in 1000 c.c. at 0° C. Hence if the vapour density were x at 0° C. it would be only $x - x/21$ at 273° C.

It follows that in order to apply Avogadro's law to determine the vapour density of a substance the observations should be made at successively higher temperatures until the value remains constant. In most cases the fall in vapour density with rise of temperature is very slight, bnt in some it is very considerable; compare sulphur (p. 213).

It is supposed that in the case of sulphur and certain other substances, there is more in this decrease of vapour density than a mere improvement of gaseous character, as will be explained a little later.

It will presently be made clear that by the chemist the determination of vapour density for ascertaining molecular weights is used solely as an indication as to which of two values is correct; for this method lacks the accuracy attainable by that which is particularly the chemist's own—gravimetric analysis. The whole system of molecular and atomic weights has been built up by use of the balance to determine chemical equivalents.

* Vapour density is distinct from specific gravity. Of course the latter decreases with rise of temperature because it is the ratio between the weight of a volume of the gas at the particular temperature and that of an equal volume of the standard gas at standard temperature and pressure. The vapour density is determined by weighing both gases at the same temperature, whatever that may be, and should be a constant.

Chemical Equivalents.—It was seen above that Dalton constructed a table of atomic weights, the figures in which represented the number of parts by weight of the respective elements which combine with one part by weight of hydrogen. These figures are what are now called chemical equivalents and are determined by analysing the compounds of the elements with hydrogen; thus, it having been found that 100 parts of the compound of sulphur with hydrogen contain 94.1 of sulphur and 5.9 of hydrogen, the chemical equivalent of sulphur is $94.1 \div 5.9 = 16$. But the majority of elements do not combine with hydrogen, or do not combine with it to form compounds which may easily be analysed with accuracy. However, nearly all combine with oxygen, and as the chemical equivalent of the latter is well established as 8, the chemical equivalent of other elements may be ascertained by analysing their oxygen compounds to find what weight of the element combines with 8 parts by weight of oxygen.

In cases where the element forms more than one compound with hydrogen or oxygen, as for instance carbon (p. 137), there may be said to be more than one equivalent. The lowest number, however, is selected; thus 3 is the equivalent of carbon, although 6 and 12 parts of it also combine with 1 part of hydrogen.

Had the chemist to concern himself with weights alone, a list of chemical equivalents would suffice; indeed, until recently no account was taken of any other numbers by the purely analytical chemist; for him the symbol of an element represented its chemical equivalent. The progress of chemical investigation, however, would have been far less rapid had not the chemist sought an insight into the actual mechanism of chemical change by aid of an atomic hypothesis, which, as explained for oxygen on p. 289, necessitates the abandonment of the chemical equivalent as the unit weight of an element that enters into chemical change, that is, the atomic weight.

Atomic Weights.—Except in certain cases which have been satisfactorily explained (as will be shown later in this work), there has never been evidence that in any compound of hydrogen the ratio between the number of atoms of H and the other element, X, is less than 1 : 1. That is to say, compounds of the formula HX_2, HX_3, &c., are not known, except as aforesaid; they are limited to the form HX. On the other hand, compounds of the types H_2X, H_3X, H_4X are quite common.

From this it is evident that (1) the atomic weight cannot be less than the equivalent; (2) the atomic weight of an element forming the compound HX must be identical with the equivalent; and (3) the atomic weights of elements forming H_2X, H_3X, and H_4X respectively, must be twice, thrice, and four times the equivalents respectively.

There are three methods for determining whether 1, 2, 3, or 4 is the factor for ascertaining the atomic weight from the equivalent.

(1) This method is best explained by an example. The vapour density of a compound of nitrogen is ascertained, as described at p. 292, to be 15, so that the molecular weight of the compound is 30. Gravimetric analysis shows that the compound contains 45.16 per cent. of nitrogen. Hence 30 parts by weight of it contain 13.55 parts of this element, that is to say, one molecule of the compound contains n atoms of nitrogen weighing 13.55. If n is one, then 13.55 is

approximately the atomic weight of nitrogen; if n is 2 the atomic weight is 6.77, and so on. It is impossible to decide the value of n from this experiment; all that can be said is that by hypothesis it cannot be less than 1, so that the atomic weight of nitrogen, according to this experiment, is not greater than 13.55 or a number very near this. Supposing, however, that many other compounds of nitrogen have been submitted to similar experiments, and it has been found that in none of them does the molecular weight contain less than 13.55 parts of nitrogen, the presumption is large that this is indeed the *approximate* atomic weight.

By analysing ammonia, the compound of nitrogen with hydrogen, it is found to contain for every part of hydrogen 4.66 parts of nitrogen; 4 66 is therefore the chemical equivalent of this element. Now 13.55 is nearly 3 times 4.66, so 3 is the factor required and $4.66 \times 3 = 14$ is the atomic weight of nitrogen.

This method consists, then, in determining the molecular weights of compounds of the element, and ascertaining how many parts by weight of the element the molecular weight contains in each case. The lowest value obtained is the *maximum* possible value for the atomic weight and comparison with the chemical equivalent gives the required factor.

(2) It was observed by Dulong and Petit (1819), from the study of elements of known atomic weight that *the quantity of heat necessary to raise the temperature of one atomic weight of any solid element is approximately the same*, or, more generally, "the atoms of all the simple bodies have exactly the same capacity for heat."

It will be remembered that the specific heat of a substance is the quantity of heat required to raise its temperature through 1° as compared with the quantity of heat required to raise the temperature of an equal weight of water through 1°; or, more concisely, the quantity of heat required to raise one part by weight of the substance 1° (referred to water as the unit). Thus, the specific heats of potassium, sodium, and lithium are, respectively, 0.1696, 0.2934, and 0.9408, these numbers representing the relative quantities of heat required to raise one part by weight of each of these elements through 1° in temperature, supposing that an equal weight of water would be raised through 1° by a quantity of heat expressed by *one*. No simple relation can be traced between these numbers, but if the quantities of heat be calculated which are required to raise *atomic* weights of these elements through 1°, the case will be different.

If 0.1696 be the quantity of heat required to raise the temperature of one part by weight of potassium through 1°, 0.1696×39, or 6.61, will represent the quantity of heat required to raise the temperature of 39 parts by weight (one atomic weight) of potassium through 1°. In the same way 0.2934×23, or 6.75, is the quantity of heat required to raise the temperature of one atomic weight of sodium through 1°; and 0.9408×7, or 6.59, is the quantity required to raise one atomic weight of lithium through 1°. Allowing for experimental error in the determination of the specific heats, these numbers, 6.61, 6.75, and 6.59, may be regarded as representing the same quantity of heat, and they are the *atomic heats* of these metals.

The *atomic heat* of an element is the quantity of heat required to raise the temperature of the number of unit weights of the solid

element expressed by the atomic weight through 1° ; it is ascertained by multiplying the specific heat by the atomic weight and is approximately a constant, 6.4.

It is obvious that since *specific heat* × *atomic weight* = 6.4, the *atomic weight* = $\frac{6.4}{\textit{specific heat}}$, and that from the equation an approximate value for the atomic weight of an element can be ascertained if the specific heat of the solid element is known.

When efforts to determine the specific heat of an element have failed, it is sometimes possible to arrive at a value for the atomic heat by a consideration of the *molecular heat* of compounds containing the element. The *molecular heat* of a compound is the quantity of heat required to raise the temperature of the number of unit weights of the compound expressed by the molecular weight, through 1°. It is supposed that the molecular heat of a compound is the sum of the atomic heats of each of the atoms which the molecule contains—a generalisation which is not fully substantiated.

Thus, the specific heat of solid chlorine is not known, but if the specific heats of the chlorides of potassium, sodium, and rubidium are multiplied by the molecular weights of these chlorides, the product in each case approaches very nearly to the number 12.69. Supposing these chlorides to contain one atom of each of their constituents, then, by subtracting the mean atomic heat (6.65) of the three metals from the mean molecular heat (12.69) of the three chlorides, a value (6.04) for the atomic heat of solid chlorine will, according to the above generalisation, be obtained.

The specific heat of barium has not been determined so that its atomic weight has not been ascertained directly by this method ; but the specific heat of barium chloride is 0.09. Barium chloride contains 68.5 parts of barium for every 35.5 parts of chlorine ; if 68.5 be the atomic weight of barium, the formula for the chloride will be BaCl, and its molecular heat 0.09 × 104 = 9.36 ; this only allows an atomic heat of 3.36 for barium, because that of chlorine is 6.0. If the atomic weight of barium be 137 the formula for the chloride will be $BaCl_2$, and the molecular heat will be 208 × 0.09 = 18.72 ; this will allow an atomic heat of 6.72 for barium, for two atomic heats of chlorine must be subtracted from 18.72. As 6.72 is more nearly normal for the atomic heat than is 3.16, the atomic weight of barium may be taken as 137.

The specific heat of all substances varies with the temperature ; this is particularly noticeable in the case of carbon, boron, silicon, and a few other elements. At low temperatures the specific heats, and therefore the atomic heats, of C, B, and Si are very low, but at higher temperatures they increase until the atomic heats are about 5.5. Thus, the specific heat of diamond at 10° C. is 0.112, corresponding with the atomic heat 1.34, whilst at 985° C. the specific heat is 0.458, corresponding with atomic heat 5.5.

All elements whose atomic weight is above 30, obey Dulong and Petit's law.

(3) On page 11 the term valency was used to express the number of atoms of hydrogen one atom of an element can combine with. It is evident that the number expressing this valency is none other than the factor now under discussion. The third method consists in studying the general chemical analogies of the element with some other element of known valency for the purpose of deciding the unknown valency.

In this respect the *isomorphism* of the compounds of the element with those of other elements of known atomic weight, and therefore of known valency, is most important. The principle of isomorphism, originally stated by Mitscherlich (1821), is that *certain elements may be substituted for each other in their crystalline compounds without alteration of the form of the crystals.* Such elements are said to be isomorphous with each other, and the crystalline compounds, in which the substitution occurs, are said to be *isomorphous compounds.* Thus, aluminium, chromium, and iron are isomorphous elements because they all form

alums of the type $KR'''(SO_4)_2.12H_2O$ (where R''' is Fe, Al, or Cr), which crystallise in octahedra, and are capable of forming *mixed crystals*, the most important criterion of isomorphism. For example, when a mixture of solutions of aluminium alum and chromium alum is allowed to crystallise, the crystals contain both aluminium and chromium in proportion varying with the conditions of crystallisation. Supposing that the valency of chromium were unknown it could be deduced from this isomorphism with aluminium. For the valency of aluminium is three, hence it is probable that the valency of chromium is also three, in which case the atomic weight of the metal is thrice its equivalent.

As an example of the application of these three methods, the following experiments may be supposed to have been performed with a view of ascertaining the atomic weight of cadmium :

(1) 0.7232 gram of cadmium bromide * was dissolved in water, and the bromine was exactly precipitated by adding a solution of silver nitrate (with the precautions necessary to an accurate result). This solution was made by dissolving 10 grams of pure silver in 1 litre of dilute nitric acid, and 57.43 c.c. were required for the precipitation. Hence 0.5743 gram of silver will combine with the bromine in 0.7232 gram of cadmium bromide ; but from the careful synthesis of silver bromide, it is known that this weight of silver will combine with 0.4254 gram of Br ; therefore the 0.7232 gram of cadmium bromide contains 0.2978 gram of Cd combined with 0.4254 gram of Br. Since the equivalent of bromine is 80, $\frac{0.2978 \times 80}{0.4254} = 56$ will be the equivalent of cadmium—that is, the number of parts by weight of Cd which will combine with one equivalent of Br. The atomic weight of cadmium must, therefore, be $56 \times n$, where n is a small integer.

(2) The vapour density of cadmium bromide was found to be 136, therefore its molecular weight is 272 ; but, according to the above analysis, this number of grams will contain 112 grams of Cd and 160 grams of Br, for these elements are present in the ratio 56 : 80. It follows that the atomic weight of cadmium cannot be greater than 112, or n cannot be greater than 2.

(3) A piece of cadmium weighing 100 grams was heated in boiling water until it had attained the temperature of the water (100° C.) ; it was then transferred to a calorimeter containing 100 grams of water at 0° C. The temperature of this water (allowing for the heat left in the calorimeter) rose to 5.3° C. Therefore the 100 grams of cadmium, in cooling from 100° to 5.3°, have lost $100 \times 5.3 = 530$ gram-units of heat,† so that in cooling through 1° C. the 100 grams would lose $\frac{530}{94.7} = 5.6$ units, or 1 gram would lose 0.056 unit—that is, the specific heat of cadmium is 0.056. But the specific heat × atomic weight will probably = 6.4, so that the atomic weight of cadmium should be $\frac{6.4}{0.056} = 113$ (nearly). This is approximately 56×2, therefore n is probably 2.

(4) Many cadmium salts are found to crystallise together with zinc salts, being isomorphous with them ; but zinc is divalent, therefore cadmium is probably also divalent, in which case its atomic weight must be twice its equivalent, or 112.

With regard to the *standard for the atomic weights*, it may be said that many chemists prefer to fix arbitrarily 16 as the atomic weight of oxygen, rather than to adhere to Dalton's standard—viz., H = 1. The reason for this is that the equivalents of the elements are far more frequently determined from oxygen-compounds than from hydrogen-compounds, because the former are both more numerous and better capable of exact analysis.

Atomicity of Molecules.—The following paragraphs deal with methods of ascertaining the number of atoms in a molecule, that is, the *atomicity* of the molecule.

* It will be evident that the analysis of any compound of the element with another element of well-established equivalent will serve to fix the equivalent of the first element.

† No allowance is here made for the slight alteration in the specific heat of water with rise of temperature.

Considering first the atomicity of elementary molecules, the molecular weight having been determined from the vapour density and the atomic weight from the chemical equivalent, the atomicity is ascertained by simply dividing the atomic weight into the molecular weight. For instance, the vapour density of nitrogen being 14, and its atomic weight also 14, its atomicity is two—there are two atoms in the molecule; it is diatomic; its molecular symbol is N_2.

In the case of certain elements, the type of which is the newly discovered argon, there is difficulty in ascertaining the atomic weight because the element shows so little tendency to combine that the equivalent cannot be determined. A method exists whereby it is possible to decide whether an element of this kind is monatomic, diatomic, or polyatomic; it depends on the following considerations: The amount of heat required to raise the temperature of an ideal gas through 1° C. should be that expended in increasing the kinetic energy of its molecules, provided the gas is not allowed to expand, that is, if its volume is kept constant. If the gas is allowed to expand the molecules do work in overcoming the external pressure, and the heat required to raise the temperature 1° C. will be more than that necessary to increase the kinetic energy by an amount equivalent to the work done. In the former case the pressure of the gas increases when it is heated, while in the latter case it remains constant. It follows that the specific heat of a gas at constant pressure, Cp, is greater than that of the gas at constant volume, Cv. While Cp is easily determined, Cv is very difficult to determine; but the ratio Cp : Cv may be calculated, from the kinetic theory of gases, to be 1.66. A discussion of the calculations cannot be entered upon here, but it will be obvious from what was said at p. 291 that if the molecular weight of the gas be considered, the increase in kinetic energy will be proportional to $mw^2/2$, while the work done in overcoming the external pressure is proportional to $mw^2/3$. Hence, while Cv is measured by the former value, Cp is measured by $(mw^2/2 + m\,w^2/3)$ and the ratio of the latter to the former 5/6 : 1/2 or 1.66 : 1.

Now experimental methods have been devised for determining the ratio Cp : Cv, chief of which is that depending on the velocity (u) of sound in the gas for which the ratio is to be ascertained. The velocity is given by the equation $u = \sqrt{kp/d}$, where p is the pressure, d the density, and k the ratio Cp : Cv. The velocity of sound in air is a well-known experimental constant, and therefrom k is found to be 1.4 for air. By filling a glass tube, clamped at one end, with a gas and rubbing the tube so as to produce a musical note, the wave length of the note can be ascertained if the tube contain a dust capable of marking the nodes by the disturbance it suffers. By comparison of this wave length with that known for the note in air, the value of u, and therefore of k, for the gas may be calculated.

In gases that are known to have diatomic molecules, $k = 1.4$—that is, the specific heat at constant volume is more than it would be in the ideal gas. The assumption is that in a diatomic gas, the atoms in the molecule have a movement relative to each other, an intra-molecular motion, which is increased by heat. Thus heat would be absorbed which would not increase the kinetic energy of the moving molecules.

The method in question, therefore, consists in ascertaining the value Cp : Cv for the gas the atomicity of whose molecules is to be ascertained. If this ratio is 1.66 the molecules are monatomic; if it is 1.4 the molecules are diatomic. For polyatomic gases the ratio is still lower. Mercury vapour and the gases of the argon group are found by this method to be monatomic.

As already indicated (p. 294), the vapour density of some elements decreases as the temperature rises. It follows that the atomicity of the molecules decreases; thus, sulphur vapour at 480° C. has a density of 95.1, which, divided by 32, the atomic weight of sulphur, gives S_6 as the molecular symbol; but at 1000° C. the density falls to 32.1, giving S_2 for the molecular symbol. It is supposed that in such cases the molecule suffers a dissociation as the temperature rises quite analogous to that which undoubtedly occurs in the case of many compound molecules, and noticed at page 86.

The elements may be classified in this respect as follows: (1) Those whose

vapour densities are identical with their atomic weights at all temperatures:* H, O and N are the chief of these. Since M = 2D, the molecular weights of these atoms must be twice their atomic weights, and the molecule must therefore contain two atoms, it is diatomic at all temperatures. (2) Those whose vapour densities are identical with their atomic weights at low temperatures but become one-half at high temperatures. These are Cl, Br, I; their molecules are diatomic at low temperatures but monatomic at high temperatures. (3) Those whose vapour densities are one-half of their atomic weights at all temperatures, so that their molecular weights are identical with their atomic weights at all temperatures. These are Na, K, Zn, Cd, Hg, A, He. Their molecules are monatomic at all temperatures. (4) Those whose vapour densities are twice their atomic weights at low temperatures but identical with them at high temperatures. Such are P, As, Sb. Since M = 2D, the molecular weights of each of these gaseous elements must be four times their atomic weight at low temperatures, but only twice at high temperatures. They are tetratomic at low, but diatomic at high, temperatures. (5) Those whose vapour densities are a greater multiple than twice their atomic weights at low temperatures, becoming equal to their atomic weights at high temperatures. Sulphur is the only example.

Turning now to the determination of the atomicity of a compound molecule, that is, the selection of the formula for the compound, this resolves itself into three steps:

(1) Quantitative analysis of the compound to determine the percentage composition of it. Here a distinction must be drawn between a *proximate* analysis and an *ultimate* analysis. For instance, a sample of beer may be analysed to determine the percentage of alcohol, water, hop-extract, &c., in it; this is a proximate analysis. If the operations were directed to the determination of the carbon, hydrogen, oxygen, &c., in the beer—that is to say, its ultimate constituents—an ultimate analysis would have been performed. Taking alcohol as an example, the result of an ultimate analysis would be, carbon 52.16 per cent., hydrogen 13.04 per cent., oxygen 34.80 per cent. As these numbers add up to 100 no other element can be present.

(2) Division of the percentage of each element by the atomic weight of the element to ascertain the relative number of atoms of each in the compound.

In the case of alcohol the following figures would be obtained:

52.16	divided by	12	gives	4.34	atomic weights of	carbon.
13.04	,,	,,	1	,,	13.04	,,	,,	hydrogen.
34.80	,,	,,	16	,,	2.17	,,	,,	oxygen.

In its lowest terms the ratio 4.34 : 13.04 : 2.17 is 2 : 6 : 1; that is, the atoms of C, H and O are present in the molecule of alcohol in this ratio. An *experimental* or *empirical formula* for alcohol is thus obtained, and it is evidently C_2H_6O. This, however, may not be the formula for the molecule or the *molecular formula*. It is certainly the minimum formula, for by hypothesis it is impossible for the molecule to contain half an atom, as would be the case if the formula be written $CH_3O_{\frac{1}{2}}$. But the true formula may be a multiple of C_2H_6O, such as $C_4H_{12}O_2$ or $C_6H_{18}O_3$—all that is known so far is that the *ratio* of C:H:O must be 2 : 6 : 1.

(3) The vapour density of the compound is determined. It will be obvious that this settles the molecular formula, or the atomicity of the molecule. For M = 2D, so that if the molecule is C_2H_6O the vapour density must be $\frac{12 \times 2 + 1 \times 6 + 16 \times 1}{2} = 23$; if it is $C_4H_{12}O_2$ the vapour

* The temperatures referred to in this classification range from 100° C. to 1700° C.

density must be $\frac{12 \times 4 + 1 \times 12 + 16 \times 2}{2} = 46$. Now the determination of the vapour density of alcohol, as described at p. 293, gives a number near 23; therefore the molecular weight is 46 and the molecular formula is C_2H_6O, 9 atoms in the molecule.

Dissociation.—The only difficulty in following the foregoing steps for determining the molecular formula for a compound, provided that this is volatile, is in the doubt which sometimes exists whether the vapour or gas into which the compound is converted by heat is indeed the same compound. The gas produced by the vaporisation may consist of products of *decomposition* or of *dissociation* of the compound. The difference between these two phenonena has already been explained (p. 86). An example will make clear how dissociation affects the determination of molecular formulæ. The ultimate analysis of ammonium chloride shows that its empirical formula is NH_4Cl, and this must be the minimum molecular formula, because the molecule cannot contain less than one atom of N or one atom of Cl. A determination of the vapour density of ammonium chloride, however, gives the number 13.35, corresponding with molecular weight 26.7. Now, the formula NH_4Cl corresponds with molecular weight $14 + 1 \times 4 + 35.5 = 53.5$ or double that found from the vapour density, which indeed corresponds with the impossible formula $N_1H_2Cl_1$.

The experiment cited at p. 86 shows that the vapour of ammonium chloride consists not of this compound but of a mixture of ammonia, NH_3, and hydrogen chloride, HCl. That is, instead of being composed of NH_4Cl molecules, the vapour consists of a mixture of $NH_3 + HCl$ molecules. Unless the vapour itself had been tested this change would not have been detected, for it is a dissociation, not a decomposition, so that when the vapour is cooled the ammonium chloride is re-formed, just as water is obtained again when the steam from it is condensed.

To make clear how this dissociation affects the vapour density, it must be explained that ammonium chloride is found to be produced when *equal* volumes of NH_3 and HCl are mixed. Hence the dissociated vapour of ammonium chloride must consist of equal volumes of these gases. Now a mixture of gases in equal volumes always has a vapour density which is the mean of the vapour densities of the constituent gases. In this case the vapour density of NH_3 being 8.5, and that of HCl 18.2, that of the mixture would be half the sum of these values, or 13.35.

Classification of the Elements—The Periodic Law.—It has been already shown that the elements may be classified into groups which contain individuals possessed of similar chemical properties. Newlands, in 1864, pointed out that when the elements are arranged in the order of their atomic weights, this similarity is seen to exist between every eighth element, the first being similar to the eighth, the second to the ninth, and so on (*law of octaves*). In 1869 Mendeléeff and Lothar Meyer made a similar discovery.

In seeking for a basis for a classification of the elements, it is natural that the chemist should turn to the most strictly chemical property of the elements, namely, their tendency to combine with each other. Mendeléeff has pointed out that the limit to this tendency is expressed by saying that one equivalent of an element never com-

bines with more than eight equivalents of another element. If oxygen and hydrogen be taken as typical elements, it will be noticed that there are never more than four atoms of oxygen or four atoms of hydrogen united to one atom of an element. Furthermore, the sum of the equivalents of O and H, which can combine with one atom of an element is eight. Thus, if an element R forms as its highest salt-forming oxide* a compound of the type RO_2, it will form a hydride RH_4; if an oxide, RO_3, a hydride, RH_2, and so on. For example, N forms N_2O_5 as its maximum oxide—that is, a compound of five equivalents of oxygen with one atom of nitrogen—and its maximum hydride is NH_3; S forms SO_3 (6 equivalents of oxygen), and SH_2. Cl forms ClH, so that its highest salt-forming oxide should be Cl_2O_7 (7 equivalents of O to 1 atom of Cl), which, however, is only known in such compounds as $K_2O.Cl_2O_7 = 2KClO_4$.

It follows that there are eight types of higher salt-forming oxides, viz.: R_2O, R_2O_2, R_2O_3, R_2O_4, R_2O_5, R_2O_6, R_2O_7, and R_2O_8.

Those elements which form higher salt-forming oxides of the same type are alone analogous. If this proposition be admitted, the elements must be classified in eight groups. Such a classification reveals the fact that when the elements are arranged in the order of their atomic weights, they follow the same order as that of their higher oxides, so that the valency of the elements towards oxygen returns to the same value at every eighth element, that is, *periodically*. This return is noticeable in the case of all other properties of the elements which have been accurately examined, that is to say, the *properties of the elements are periodic functions of their atomic weights*. In general terms, *if the elements be arranged in the order of their atomic weights, the properties of consecutive elements will be found to differ, but the properties will return to approximately the same value at definite periods.*

Such an arrangement of the elements is shown in the appended table:

Group . .	i.	ii.	iii.	iv.	v.	vi.	vii.	viii.
Series 1 .	H ·	—	—	—	—	—	—	He
,, 2 .	Li ·	Be ·	B ·	C ·	N ·	O ·	F ·	Ne
,, 3 .	Na ·	Mg ·	Al ·	Si ·	P ·	S ·	Cl ·	Ar
,, 4 .	K ·	Ca ·	Sc ·	Ti ·	V ·	Cr ·	Mn ·	Fe : Co.Ni.Cu
,, 5 .	·(Cu)	· Zn	· Ga	· Ge	· As	· Se	· Br	Kr
,, 6 .	Rb ·	Sr ·	Y ·	Zr ·	Nb ·	Mo ·	— .	Ru : Rh.Pd.Ag
,, 7 .	·(Ag)	· Cd	· In	· Sn	· Sb	· Te	· I	Xe
,, 8 .	Cs ·	Ba ·	La ·	Ce ·	Pr ·	Nd ·	Sa ·	— — — —
,, 9 .	· Gd	. —	· Tb	. —	· Er	. —	· Tu	
,, 10 .	— .	— .	Yb ·	— .	Ta ·	W ·	— .	Os : Ir.Pt.Au
,, 11 .	·(Au)	· Hg	· Tl	· Pb	· Bi	. —	. —	
,, 12 .	— ·	— .	— .	Th ·	— .	U ·	— .	
Higher oxide type . .	R_2O	R_2O_2 (RO)	R_2O_3	R_2O_4 (RO_2)	R_2O_5	R_2O_6 (RO_3)	R_2O_7	R_2O_8 (RO_4)
Hydrides .				RH_4	RH_3	RH_2	RH	

* Capable of behaving as an anhydride or as a base.

In drawing up this table two main difficulties occurred. In the first place, Co, being next to Fe in atomic weight, should have been written in group i.; but neither this metal nor Ni shows any analogy with the elements in group i. Cu, on the other hand, shows some analogy with the elements of both group viii. and group i., consequently its true position is somewhat doubtful. Thus Co and Ni have to remain in group viii., an arrangement also necessary in the case of Rh, Pd, Ir, and Pt.

Within the last few years much difficulty has arisen owing to the discovery of the helium and argon group of elements, as these do not appear to form any chemical compounds and therefore have no valency. In the foregoing table they are placed in group viii. pending a more satisfactory elucidation of their probable position.

In the second place, the element Ru, which is next in atomic weight to Mo, should come in group vii., but its position there is untenable, because its higher oxide is of the type RO_4 and not R_2O_7. Consequently, Ru must be placed in group viii., whilst the position in group vii. remains vacant. Thus it is not always possible to locate each element in the table immediately succeeding the next lower in atomic weight, so that a certain number of blanks must be left. Where such blanks occur elements are believed to exist, but to be as yet unknown. Credence is afforded to this view by the fact that the number of such blanks was larger when the table was first drawn up, some of these spaces having been since filled by the discovery of elements (such as Ga, Ge, and Sc), the atomic weights of which showed that they were the missing elements.

It will be found that elements in the same group, and in even series, are completely similar to each other, as, for example, Ca, Sr, and Ba; this is also the case with the elements in the same group and in odd series, such as P, As, and Sb. The members of the odd series, however, do not so closely resemble those of the even series, though in the same group. Thus, Ca and Zn have far fewer properties in common than have Ca and Sr. It seems, then, that the periodic return of properties to the same value only occurs after two series have been traversed, so that each *period* of the table is constituted by two series; thus, K, Rb, and Cs resemble each other very closely. It will be seen that since this is the case, each group must consist of two sub-groups, indicated in the table by the setting of the symbols in two vertical lines in each group.

The members of these sub-groups or *families* resemble each other more closely than do the members of a group taken as a whole. Whilst this is true of the elements which follow Na, it is not true up to this point; thus, Be is more nearly allied to Mg than to Ca; B to Al than to Sc; and C to Si than to Ti. These elements, therefore, do not appear to be in their right places, a difficulty which is met by supposing that they, and those from Na to Cl (inclusive) constitute two short periods; these elements have been termed the *typical elements* of the table.

It is only possible here to call attention to a very few of the properties of the elements which return periodically to about the same value. The elements of the same family form oxides which, when bases, are of the same order of basicity and, when acid oxides, of the same order of acidity; this is well illustrated by K, Rb, Cs; Ca, Sr, Ba; P, As, Sb.

The *specific gravities* (mass of unit volume) of the elements exhibit a periodicity.

Instead of comparing specific gravities it is better to compare *atomic volumes* (or number of unit volumes in the atomic weight). The atomic volume of an element is the quotient of its atomic weight divided by its specific gravity at the melting-point, A/d (at melting-point). Those elements which are most chemically active have the lowest specific gravities and therefore the highest atomic volumes; thus it is found that the atomic volume falls from the beginning to the middle of a period, but rises again from the middle to the end; for instance, the atomic volume of K is 45, of Ni 6.8, and of Br 26. In the same family the atomic volume rises with the atomic weight; *e.g.*, Li = 12, K = 45, Rb = 57, Cs = 71. Similar relations are maintained between the *molecular volumes* (molecular weight divided by specific gravity) of the oxides and of some other compounds of the elements.

The same periodic fluctuation is to be noted in the melting-points, the electro-positiveness, the brittleness and the ductility of the elements, and extends to the colour of their salts. If, therefore, the atomic volumes be plotted on a curve, the same curve will apply to many other of the properties.

The Periodic Table has found a twofold application: (1) It has served to enable chemists to foretell the existence and properties of elements which have subsequently been discovered; (2) it has afforded a means for deciding the atomic weights of some elements.

An example of the first of these is the prophecy by Mendeléeff of the existence and properties of germanium: the principle upon which such predictions are made, is that *the properties of an element are approximately the mean of those of the four elements which immediately surround it*. There was a vacancy in the table between Si and Sn; Mendeléeff termed the element which had to be discovered to fill the gap, ekasilicon (eka is "one" in Sanscrit). According to the above principle, ekasilicon when discovered should have properties identical with the mean of those of Si, As, Sn, and Ga; but Ga was itself unknown at the time, so Mendeléeff had to use Zn as a member of the quorum. The mean of the atomic weights of these four elements is 71.5, so that this would be the atomic weight of ekasilicon; that found for germanium is 72. Ekasilicon (Es) would probably form two oxides, EsO and EsO_2, an acid oxide; for although SiO is not known, SnO is known, and both SiO_2 and SnO_2 are stable, acid oxides; GeO_2, an acid oxide, is well known, and GeO probably exists. $EsCl_4$ and $EsCl_2$ should exist, because $SnCl_4$ and $SnCl_2$ exist, but $GeCl_2$ should be less stable than $SnCl_2$, for $SiCl_2$ is not known. As a fact, both $GeCl_4$ and $GeCl_2$ exist, the latter being less stable than $SnCl_2$. Further, the boiling-point of $EsCl_4$ should be the mean of those of $SnCl_4$ and $SiCl_4$—namely, 88.5°; it is found to be 86°.

The second application of the table is illustrated by the fixation of the atomic weight of beryllium. The equivalent of beryllium is 4.5, and its atomic weight was at first said to be 13.5, because its oxide was supposed to be Be_2O_3 on account of its similarity to Al_2O_3. With this atomic weight, however, this element would have to follow carbon in the periodic table, a position certainly at variance with its properties. It was therefore suggested that its atomic weight is really 9, in which case its oxide would be BeO and the element would fall into the then vacant place in group ii., a position which has since been confirmed by the determination of the vapour density of $BeCl_2$, from which the maximum atomic weight of 9 is obtained.

The Measurement of Chemical Affinity.

Chemical affinity is a name conveniently employed to designate the unknown force by which chemical change is effected.

Energy is that fundamental property which, in addition to *mass*, is possessed by every kind of matter, and for the present purpose it may be defined as ability to effect a change in the relative position of masses of matter, be they molar, molecular, or atomic. It is of several kinds, of which chemical energy is one. Heat energy, electrical energy, kinetic energy (or that resident in moving matter), and potential energy (or that resident in matter by virtue of its position), are other kinds of energy.

The nature of chemical energy is unknown; but it may be compared with potential energy, for it appears to depend upon the position of the matter in which it resides. Thus a mixture of hydrogen and oxygen may be said to possess a potential energy due to the position of close proximity of the molecules; for, just as the potential energy of a stone on the edge of a cliff requires an impulse

in order to convert it into another form of energy—the kinetic energy of its fall to the foot of the cliff—so the potential energy of a mixture of hydrogen and oxygen requires an impulse, such as the heat of an electric spark, in order to convert it into another form of energy—heat energy.

The potential energy of a stone on a cliff is measured by multiplying the force which impels the stone to fall to the foot of the cliff by the space through which it has to fall, so that potential energy = force × space. Chemical energy may also be regarded as composed of two factors; one of these is, perhaps, chemical affinity, the other is unknown.

It is not necessary to know the force impelling the stone to fall, or the space through which it falls, in order to ascertain the potential energy of a stone on a cliff. If the stone be allowed to fall, and steps be taken to receive it in such a manner that all the heat generated by its impact with the earth is measured, then, by the principle of the Conservation of Energy,* the potential energy can be calculated from this heat, which is exactly equivalent to it. (The *mechanical equivalent of heat* is: one gram-unit of heat = the energy represented by one gram falling through 42.350 centimetres.)

It should be equally possible to measure the chemical energy of a mixture of hydrogen with oxygen by ascertaining the quantity of heat evolved during the combination of the gases, and although this method would not necessarily measure the chemical affinity of the hydrogen for the oxygen, yet the value obtained would probably be proportional to this affinity.

There are two methods by which a force may be directly measured: (1) A force of known magnitude may be brought to bear upon the force to be measured in such a manner that the two are in equilibrium. The two forces will then be equal. Such a method may be called a *static method*, and would be employed if a force of known value were brought to bear upon a falling stone so as to bring it to rest; the force of the stone would then be equal to the opposing force; (2) by measuring the velocity of a moving mass in successive seconds, the force impelling the motion is measured by the change which occurs in this velocity. This may be called a *kinetic method*.

The attempts which have been made to measure chemical affinity involve methods analogous to these two methods of measuring dynamical force. But the attempt to measure the chemical energy of chemical reactions by ascertaining their heat changes, and thus to obtain measurements which may be regarded as proportional to chemical affinity, has been made to a much greater extent than have attempts to apply the static or the kinetic method; the measurement of chemical energy by measuring thermal changes will therefore be considered first.

Thermochemistry is that branch of the science of chemistry which deals with the study of the thermal changes accompanying chemical reactions. The prime object of the study is to obtain relative measurements of the chemical affinities inducing the reactions.

Attention has been called in the preceding pages to some of the principles of thermochemistry, but they may aptly be summarised here. (1) Every chemical change is accompanied by a thermal change, which is a constant quantity. (2) The thermal change occurring during the combination of elements to form a compound is called the *heat of formation* of the compound. It is generally a positive quantity, that is, heat is evolved—the compound is *exothermic;* sometimes, however, it is a negative quantity, that is, heat is absorbed—the compound is *endothermic*. (3) The thermal change occurring during the decomposition of a compound is called the *heat of decomposition* of the compound. (4) The heat of decomposition of a compound is identical with, but of opposite sign to, the heat of formation of that compound.

* This principle may be expressed thus: In any space the total quantity of energy remains the same, although the energy may be transferred from one part of the space to another, or transformed from one kind of energy into another. An example of the principle is furnished by the firing of a mixture of H_2+O in a vessel from which loss of heat is impossible. There is the same quantity of energy in the vessel before the explosion and after it, but after the explosion the energy is in the form of heat energy instead of chemical energy.

The last proposition follows from the principle of the conservation of energy (see foot-note, p. 305). The potential energy of a mixture of elements is lost to the system in the form of heat energy when the elements combine; and in order that the elements may be again imbued with the same potential energy, heat energy, or some other form of energy, must be restored to the system.

The measurement of the thermal changes of chemical reactions is effected by causing the reaction to occur in a closed chamber which is immersed in a *calorimeter*, such as that described at p. 164.

The heat of formation of a compound is expressed thus: $H,Cl = 22{,}000$, meaning that the combination of 1 gram of hydrogen with 35·5 grams of chlorine *evolves* 22,000 gram-units of heat. Again, $N,O_2 = -7700$, means that when 14 grams of nitrogen combine with 32 grams of oxygen, 7700 gram-units of heat are *absorbed*. Again, $H_2O,SO_3 = 21{,}320$ means that when 18 grams of water combine with 80 grams of SO_3, 21,320 gram-units of heat are evolved. The heat of decomposition is expressed similarly, but with reversed signs, thus: $-H,Cl = -22{,}000$; $-N,O_2 = +7700$.

The value obtained in a calorimeter for the thermal change of a reaction is not necessarily the thermal change due to that chemical reaction whose heat is to be measured. Allowance must frequently be made for secondary chemical reactions and for changes of physical state.

Two examples may be quoted in order to make this clear:

(1) 80 grams of SO_3 were mixed with a large excess of water (the quantity being known) with the view of ascertaining the thermal change SO_3, H_2O. The value obtained was 39,177; but this obviously includes two thermal changes: (*a*) that due to the combination of 80 grams of SO_3 with 18 grams of H_2O, and (*b*) that due to the combination of the H_2SO_4 produced with an excess of water. When sulphuric acid is diluted with water in a calorimeter, it is found that heat continues to be evolved until the weight of water amounts to about thirty-six times that of the sulphuric acid (corresponding with the formula $H_2SO_4.200H_2O$); this thermal change amounts to 17,857 gram-units per 98 grams of H_2SO_4, and must be subtracted from that observed on mixing 80 grams of SO_3 with a large excess of water in order to arrive at the value SO_3,H_2O. This now becomes 21,320. A similar action of excess of water has to be taken into account in many cases, and it is customary to use the symbol Aq for such an excess. Thus, $SO_3,Aq = 39{,}177$ means that when SO_3 is dissolved in so much water that the addition of a further quantity will produce no further thermal change, 39,177 gram-units of heat are evolved.

(2) 0·1 gram of hydrogen and 0·8 gram of oxygen were mixed and fired in a calorimeter, the final temperature of which was 20° C. The gram-units of heat evolved by the reaction (calculated from the rise of temperature) amounted to 3418. This corresponds with $H_2,O = 68{,}360$. But since we know of at least three sources from which this thermal change is derived, this value cannot be regarded as expressing the amount of heat energy equivalent to the chemical energy of the combination. The first source is the chemical energy of the combination. The second and third sources are due to the change of aggregation which occurs after the gases have combined.

The steam produced by the combination of H_2+O occupies two-thirds of the volume previously occupied by the mixed gases; now the contraction of the volume of a gas always involves a transformation of some of the kinetic energy of the gas into heat energy; in other words, heat is evolved by the contraction. It is unreasonable to suppose that the condensation of H_2+O into steam is an exception to this rule, so that the heat evolved by this condensation must be allowed for in the present case; a value for it, however, can only be calculated when the kinetic energy of the molecules of hydrogen and oxygen, and that of the molecules of steam are known. The method by which these kinetic energies are calculated cannot be given here; suffice it to say that the difference between

the kinetic energy of 18 grams of H_2+O and that of 18 grams of steam has been calculated to be equivalent to 193 gram-units of heat.

Of much greater importance than the above item, is the difference between the kinetic energies of steam molecules at 100° C. and water molecules at the same temperature. This difference is well known, and is expressed by the heat of condensation of steam. One gram of steam at 100° C. evolves 536·5 gram-units of heat in becoming water at 100° C. Therefore 18 grams will evolve 9666 gram-units. In the calorimeter the water formed by the reaction does not remain at 100° C., but cools to 20° C. before the temperature of the outside water in the calorimeter is measured. In cooling from 100° to 20°, 1 gram of water loses 80 gram-units of heat (supposing that the specific heat of water is constant over this range of temperature); therefore 18 grams of water lose 1440 gram-units.

From these remarks it will be seen that of the total 68,360 gram-units evolved by the reaction in the calorimeter, 11,299 are due to the changes of aggregation, namely, 193 to the contraction of H_2+O to steam, 9666 to the condensation of the steam to water at 100° C., and 1440 to the cooling of water from 100° C. to 20° C. By deducting these 11,299 units from the total, 57,061 gram-units are obtained as the thermal equivalent of the potential chemical energy of a mixture of hydrogen and oxygen, rendered kinetic by the combination.

It must be remembered that even when every allowance has been made for such secondary reactions and such changes of aggregation, it is by no means certain that the thermal value obtained represents the energy of combination of the *atoms* concerned in the chemical change. If the hypothesis be adopted that the molecules of hydrogen and oxygen, for example, must be separated into their constituent atoms before combination can occur, it must be admitted that some energy is absorbed in this preliminary process. This energy will become potential in the atoms, and may or may not be completely rendered kinetic, and therefore evolved as heat, when the atoms combine to form molecules of water. Thus it may happen that the heat evolved in the combination of hydrogen and oxygen, is only the excess of that due to the combination of the atoms of H and O over that absorbed by the decomposition of the molecules of H and O into atoms. It will be obvious, however, that for all practical purposes, such as for the calculation of the calorific value of a gaseous fuel (see Fuel), the calorimetrical value for the combination of hydrogen and oxygen is a perfectly correct one, inasmuch as the gases employed in the experiment are in the same condition as those used in practice.

The heat of formation of many compounds cannot be directly determined because the compounds are not formed by the direct combination of their elements. In such cases the value is calculated by methods which can receive but short notice here.

The principle underlying one of these methods is that the thermal change of any reaction in which a compound AB is concerned, must be smaller or greater* than the thermal change of a reaction—having the same products—in which the *constituents* A and B are concerned, by the heat of formation of AB. For example, the combustion of CH_4 is thermally expressed thus: $CH_4,O_4=211{,}930$ gram-units; but it is supposed that the mechanism of this combustion consists in the decomposition of CH_4 into its elements which are then burnt, and it will be at once evident that in the two reactions, $CH_4+O_4=CO_2+2H_2O$ and $C+H_4+O_4=CO_2+2H_2O$, the heat evolved in the latter will differ from that evolved in the former by an amount representing the heat of decomposition of CH_4. Now $C,O_2=96{,}960$ gram-units when solid carbon is burnt,

* Accordingly as AB is exothermic or endothermic.

and $H_4,O_2 = 136,720$ gram-units for gaseous hydrogen; therefore $(C + H_4),O_4 = 96,960 + 136,720 = 233,680$ gram-units. But $CH_4,O_4 = 211,930$, that is, the heat of combustion of the constituents of CH_4 exceeds that of CH_4 itself by 21,750; consequently, CH_4 must have *absorbed* this amount of heat in being decomposed into its elements before these were burnt. Thus it is concluded that marsh gas is an exothermic compound, and that $C,H_4 = 21,750$ gram-units, supposing that the gas were produced from solid carbon and gaseous hydrogen.

Another instance: N_2O cannot be formed directly from its elements, but the heat of combustion of carbon in the gas is easily determined, and it is found that the reaction $C + 2N_2O = CO_2 + N_4$ evolves 133,900 gram-units. Now this reaction involves the decomposition of $2N_2O$ and the formation of CO_2, so that the heat evolved should be smaller or greater than that evolved in the reaction of $C + O_2 = CO_2$ by the heat of decomposition of $2N_2O$. Since $C,O_2 = 96,960$, the heat of decomposition of $2N_2O$ must be $133,900 - 96,960 = 36,940$ gram-units, and that of N_2O must be 18,470 gram-units; in other words, nitrous oxide *evolves* heat in its decomposition, and is therefore an endothermic compound, or $N_2,O = -18,470$.

Another method for indirectly determining the heat of formation of a compound depends upon the fact that the total energy change in a reaction is the same whether the reaction occurs in one stage or in several. This is only an application of the principle of the conservation of energy; the total energy of a stone falling to the earth is the same whether the fall occur in one stage or in several. An example of the method is furnished by the determination of the heat of formation of H_2SO_4. This compound cannot be made from its elements directly, but the heat of the reaction $H_2O + SO_2 + O = H_2SO_4$ is determinable, and that of $H_2 + O = H_2O$, and of $S + O_2 = SO_2$, are well known. The total heat evolved in the formation of H_2SO_4 will be the same whether the change is in one stage, $H_2 + S + O_4 = H_2SO_4$, or in three, viz., (1) $H_2 + O = H_2O + 68,360$; (2) $S + O_2 = SO_2 + 71,080$; (3) $H_2O + SO_2 + O = H_2SO_4 + 53,480$; consequently, $H_2,S,O_4 = 68,360 + 71,080 + 53,480 = 192,920$.

From what has been said, it will be apparent that the thermal changes of chemical reactions, as they are at present determined, cannot be regarded with certainty as equivalent to the total chemical energy concerned in the reaction. They cannot, therefore, be said to be an absolute measure of the chemical affinity of elements for each other.

Nevertheless, the thermochemical data which have been accumulated, and are to be found in most books of chemical constants, are useful aids to the chemist when it is remembered (1) that endothermic reactions rarely occur save by the application of external energy (generally applied in the form of heat energy); (2) that of two exothermic reactions, that is more likely to occur, under ordinary conditions, which is the more exothermic; and (3) that of two exothermic compounds that which is the more exothermic is the more stable.

For example, it is seen from the thermal values $Ca,O = 132,000$ and $C,O_2 = 96,960$ that it is not probable that carbon will reduce CaO at any but a very high temperature; for the reaction $2CaO + C = CO_2 + Ca_2$ is highly endothermic, since it involves the heat of decomposition of 2CaO (−264,000), and the heat of formation of CO_2, leaving a balance of −167,040 gram-units. As a fact the reaction does not occur at any temperature hitherto attained, for although in the manufacture of calcium carbide reduction of CaO may be said to occur, it must be aided by the affinity of Ca for C at the high temperature used.

Again, in any competition between chlorine and bromine for hydrogen, chlorine may be expected to prevail, for H,Cl = 22,000 and H,Br = 13,500. HCl is the more stable of these two because it is the more exothermic.

In attempting to use thermal data as a guide for prophesying what will occur in a chemical reaction, it must not be forgotten that they have nearly all been determined at an initial and final temperature of about 20° C., and are only true for the elements in their usual condition at this temperature. There is no reason to suppose that the thermal change at a high temperature is the same as it is at 20° C. Thus it has been shown that the heat of formation of hydrogen iodide is negative at low temperatures, but positive at 400° C.

Static method of measuring chemical energy.—For practical purposes chemical reactions may be classified into *complete* and *reversible* reactions. The former class includes those changes in which the whole of the reacting substances is converted into the products of the reaction; for example, when a mixture of equal volumes of H and Cl is fired, the two gases combine completely and are entirely converted into HCl. A reversible reaction is of such a nature that the products of the reaction will, under a slight alteration of conditions, react with each other to re-form the original substances. Thus, when steam and iron are heated together, a reaction expressed by the equation $Fe_3 + 4H_2O = Fe_3O_4 + H_8$ occurs; but it is equally true that when hydrogen and Fe_3O_4 are heated together the reaction $Fe_3O_4 + H_8 = 4H_2O + Fe_3$ occurs. Now either of these reactions may be carried to approximate completion under certain conditions; thus, by passing steam over red-hot iron the whole of the iron can be converted into Fe_3O_4; so also by passing hydrogen over Fe_3O_4 at the same temperature the whole of this can be reduced to metallic iron. But if iron and steam be heated together in a closed vessel, the iron will never be completely oxidised. This is because the reaction is reversible, that is to say, as soon as any Fe_3O_4 and H are produced these tend to react with each other to form H_2O and Fe; in other words, the reaction $Fe_3 + 4H_2O \rightleftarrows Fe_3O_4 + H_8$, can take place in either direction at the same time, a fact expressed by the substitution of $\rightleftarrows$ for = in the equation.

It has been seen, however, that by passing steam over red-hot iron the latter can be completely oxidised—that is to say, the equation $Fe_3 + 4H_2O = Fe_3O_4 + H_8$ can be realised. This is only possible because one of the products of the reaction (the hydrogen) is in such a physical condition that it can be removed from the sphere of action (the tube in which the reaction is performed); indeed, for the complete oxidation of the iron a large excess of steam over that indicated as necessary by the equation (72 parts of steam for 168 parts of iron) must be passed through the apparatus containing the iron in order to sweep away the hydrogen. If the hydrogen could not be removed in this manner, the completion of the reaction would be impossible. The same remarks, *mutatis mutandis*, apply to the complete reduction of Fe_3O_4 by hydrogen.

A reversible reaction can only become complete when one of the products of the reaction is removed from the sphere of action. Under any other conditions the vessel in which the reaction is proceeding will contain some of each of the reacting substances, and some of each of the products of the reaction.

The question naturally arises, When iron and steam are heated in a closed vessel, so that nothing can escape from the sphere of action, how far will the reaction proceed? How much iron oxide and hydrogen will

be produced? How much steam and iron will be left? To fully appreciate the state of the case it must be realised that both the reactions expressed by the equation $Fe_3 + 4H_2O \rightleftarrows Fe_3O_4 + H_8$ are proceeding at the same time, and during the whole time, and that if the temperature be kept constant a period will soon be reached, when the amount of iron oxidised per unit time will be exactly equivalent to the amount of iron oxide reduced per unit time.

When this state of affairs prevails the equation in the direction represented by the arrow→, which may conveniently be termed the equation representing the *positive* change, will be realised to exactly the same extent as the equation represented by the arrow←(the *negative* change) is realised, per second. This is called the *equilibrium stage* of the reversible reaction, and when it is attained an analysis of the contents of the vessel will show the same proportion of iron, steam, iron oxide and hydrogen to be present, however long the vessel is maintained at the same temperature. An alteration in the temperature will cause an alteration in the extent to which either the positive or negative change will occur per second; so that with every such change of temperature a new equilibrium stage will be established, and an analysis will show a new proportion between the quantities of the four substances present.

There is another factor besides temperature which influences the quantity of each of the substances present at the equilibrium stage of a reversible reaction. This is the *mass* of any one of the substances. Thus, if iron and steam be heated in the proportion represented by the equation (168 parts of iron: 72 parts of steam) at any given temperature, exactly the same quantity of iron oxide and hydrogen will be produced as would remain undecomposed if iron oxide and hydrogen were heated in the proportion represented by the equation (232 parts of Fe_3O_4: 8 parts of hydrogen), at the same temperature. But if the mass of either the steam or the hydrogen be increased, then the quantities of steam or hydrogen present at the equilibrium stage will be altered. If the proportion of either of the constituents on the left hand of the equation be increased, the positive change will have occurred to a greater extent—that is, more Fe_3O_4 and H will have been produced —when the equilibrium stage is reached, than was the case with the former proportion. If the proportion of either of the substances on the right hand of the equation be increased, the negative change will occur to a greater extent than before. Since Fe and Fe_3O_4 are solids while hydrogen and steam are gases, the system is in this case heterogeneous, and of the four substances only the H_2O and H can intermix. Hence, here, an alteration of the proportion of Fe or Fe_3O_4 has but little effect upon the change.

This *mass action* is of great importance in chemical change, and may be generally expressed by stating that *in a homogeneous system chemical change is proportional to the active mass of each of the substances taking part in the reaction*. By *active* mass is meant the number of molecules of the substance in unit volume, such as gram-molecules per litre.

From a practical point of view mass action frequently influences chemical change, a large mass compensating a feeble affinity, it being possible for reactions to proceed which, considering the relative affinities, could not occur unless one of the products were sufficiently insoluble to be removed from the homogeneous system. Such a case will be met in the description of the manufacture of caustic soda, where the comparatively feeble affinity of lime for CO_2 is nevertheless suffi-

cient to allow the reaction $Na_2CO_3 + Ca(OH)_2 = 2NaOH + CaCO_3$ to occur in solution, because the $CaCO_3$ immediately separates from the liquid and the reaction in the left hand direction cannot, in consequence, occur so rapidly as that in the right hand direction. Nevertheless care must be taken that the active mass of the NaOH does not increase too much, for then even the precipitated $CaCO_3$ will be attacked to reproduce Na_2CO_3 and $Ca(OH)_2$. In other words, the solution must not be too concentrated.

It is not difficult to imagine the mechanism of this mass action ; the greater the number of molecules in a given space the more frequently will they come into contact with each other, and since chemical change appears to occur only between molecules in contact, the greater will be the amount of chemical change produced. In the case of steam and red-hot iron, it is obvious that the greater the number of steam molecules present, the more frequently these will come in contact with the iron, and the more oxide of iron, and consequently hydrogen, will be produced.

The subject of dissociation furnishes numerous examples of mass action.

The chemical equilibrium between two opposing reactions, such as those concerned in the action of steam on red-hot iron, should serve as a *static method* for determining chemical energy. For the equilibrium is between two chemical affinities, the one tending to produce the positive change, the other tending to produce the negative change; and the amount of each change must be proportional to the affinity which produces it; so that by analytically determining the quantities of substances present, and, therefore, the extent of the reaction, at the equilibrium stage, it should be possible to form a comparison between these affinities.

The action of steam on red-hot iron does not lend itself to the application of this method as the system is heterogeneous. But a number of double decompositions has been studied from this point of view ; they are reversible reactions and are mostly between organic compounds, so that in this place it will be useful to express them by the general form $AB + CD \rightleftarrows AC + BD$. The opposing forces which bring about the equilibrium of such a change are the sum of the affinities of A for C and B for D (say k) against the sum of the affinities of A for B and C for D (say k^1). The amount of chemical change which has occurred at the equilibrium stage is proportional to the active masses of the reacting substances, and, presumably, also to these *coefficients of affinity*, k and k^1. The amount of chemical change can be measured by chemical analysis. Suppose AB and CD be mixed in the proportion of one gram-molecule of each ; then, when equilibrium has been attained, there will be present a fraction of a gram-molecule of AC, BD, AB, and CD respectively ; and the fraction will be the same for AC and for BD, and also the same for AB and CD. Let this fraction of AC and BD be x, then that of AB and CD must be $1 - x$, for one gram-molecule was originally taken.

The active masses of AC and BD, tending to produce the negative change, are x and x, and their total effect may be represented as $x.x$ or x^2. The affinity tending to produce the negative change is k^1, so that the total force producing the negative change is $k^1 x^2$.

The active masses of AB and CD are $1 - x$ and $1 - x$, and the affinity is k; therefore the total force tending to produce the positive change is $k(1 - x)^2$.

When the equilibrium stage is reached these two forces are equal to each other, whence $k(1 - x)^2 = k^1 x^2$ or $k/k^1 = x^2/(1 - x)^2$. Thus the ratio k/k^1 can be determined, for x is determinable by analysis. For example, when acetic acid and ethyl alcohol are heated together, ethyl acetate and water are produced, the reaction being reversible. When x is determined (after no more change appears to occur), it is found to be $\frac{2}{3}$, whence, by the above formula, $k/k^1 = 4$.

By this static method the relative affinity, or *acridity*, of acids for bases has been determined. The principle of the method is to mix equivalent quantities of two acids with a quantity of base insufficient to saturate both, and to determine what proportion of the base each acid will acquire. Thus, when NaOH is mixed with HNO_3 and $\frac{1}{2}$ H_2SO_4 (equal equivalents) two-thirds of the soda combines with the nitric acid and one-third with the sulphuric acid, showing that the avidity of the

nitric acid is twice as great as that of the sulphuric acid. If the avidity of nitric acid be taken as 1, that of sulphuric acid is 0.5.

The *avidity* of an acid may be defined as the proportion of base which that acid will appropriate when equivalent quantities of the acid, a base and HNO_3 are mixed in aqueous solution. It is independent of the nature of the base. The following order of avidities is probably correct: $HNO_3 = 1$; $HCl = 1$; $HBr = 0.89$; $HI = 0.79$; $H_2SO_4 = 0.5$.

Thus, in solutions of equivalent concentration, HNO_3 and HCl must be accounted stronger acids than H_2SO_4; but the greater volatility of the two first will enable H_2SO_4 to expel them when heated with their salts.

Kinetic method of measuring chemical affinity.—This method of measuring chemical affinity consists in determining the amount of chemical change which occurs in unit time, not waiting for equilibrium to occur. This value is termed the *coefficient of velocity* of the change, and the greater this coefficient of velocity the greater the force inducing the change.

Most changes are too rapid for any determination of the coefficient of velocity, but in the class of changes known as hydrolysis (p. 265), such a measurement is possible because the change only occurs with moderate rapidity in the presence of an acid. Thus, when cane sugar is boiled with water it is very slowly converted into invert sugar; $C_{12}H_{22}O_{11} + HOH = 2C_6H_{12}O_6$; but in the presence of a dilute acid the change is much more rapid, and can be measured by determining the amount of invert sugar produced. The action of the acid is not understood, but is generally ascribed to a *predisposing affinity* of the acid for the invert sugar; this means that the invert sugar is the more readily produced because of the tendency which the acid has to form an unstable compound with it; such a compound must be soon decomposed again, because to all appearances the same amount of free acid remains in the solution after the hydrolysis as was there before.

Different acids have a different influence on the rate of the hydrolysis of cane-sugar, &c., and it is reasonable to suppose that this rapidity of action is in some way proportional to the affinity, or avidity, of the acid. By determining the velocity of hydrolysis—that is, the amount of cane-sugar which has been hydrolysed per minute—when different acids are present, the avidities of the acids may be compared. The mathematical calculations involved are somewhat complex, and cannot be discuseed here. The method yields values for the avidities of acids which are in the same order of magnitude as those determined by the static method.

A little consideration of the definition of *dissociation* (p. 86) will show that the phenomenon belongs to the same class as the reversible reactions, such as the action of steam on red-hot iron discussed above.* The contemplation of the case of phosphorus pentachloride will render this more evident. When this compound is heated above 300°C. it dissociates to a very large extent into $PCl_3 + Cl_2$, a fact discovered by attempting to determine the vapour density of PCl_5. The amount of dissociation depends on the temperature and on the active masses of the substances present. The equilibrium between the positive and negative changes of the reversible reaction $PCl_5 \rightleftarrows PCl_3 + Cl_2$, occurs when the same quantity of PCl_5 is dissociated and associated in unit time, and this will vary for every temperature.

Since PCl_5, PCl_3, Cl_2 each represents 2 vols., the total active mass tending to produce the negative change is twice as great as the active mass tending to produce the positive change. If the vessel containing the three substances at the equilibrium stage be diminished in size, that is, if the pressure be increased, the active masses of all three will be increased; for there will now be more of each in unit volume. Suppose the pressure to have been trebled, the active mass of each will have

* Recently, certain phenomena have been noted, which seem to indicate that dissociation of a compound can occur in the reverse sense to that usually observed, namely, as the compound cools. The behaviour of ruthenium tetroxide (*q.v.*) may be cited as an example. Further search for phenomena of this kind is needed.

been trebled; but the negative change is proportional to the active masses of PCl_3 *and* Cl_2 so that it will have become nine-fold, whilst the positive change is only dependent on the active mass of the PCl_5 and will therefore have only been trebled. Consequently the negative change will predominate over the positive change, and a new equilibrium will be established—in other words, the dissociation will be diminished. Similar reasoning may be applied to all cases of the dissociation of gases, when it will be found that if the products of dissociation have a larger total volume than the volume of the substance undergoing dissociation, *an increase of pressure will diminish the dissociation, whilst a diminution of pressure will increase it.*

The effect of introducing one of the products of the dissociation into the vessel at the equilibrium stage would be to increase the active mass of that product and to increase the negative change, that is, to cause association. Thus, if PCl_3 were introduced there would immediately be a reproduction of PCl_5. Advantage may be taken of this to prevent dissociation from occurring at all; for instance, if PCl_5 be heated in a vessel containing PCl_3, it will not undergo dissociation until a much higher temperature than that at which it dissociates when heated alone.

The extent to which PCl_5 has undergone dissociation is calculated from the observed vapour density. Let x be the percentage of molecules which have undergone dissociation; then $100 - x$ is the percentage still associated. But the x molecules have become $2x$ molecules when dissociated. Therefore 100 molecules have become $100 - x + 2x = 100 + x$ molecules after partial dissociation, so that the volume is increased in the ratio $100 : 100 + x$. The vapour density, however, has decreased inversely to the volume. If d be the vapour density before, and D that after, partial dissociation, then $100 : 100 + x :: D : d$ or $x = \frac{100(d - D)}{D}$.

The similarity between changes which are generally distinguished as physical and chemical is well seen by a comparison of certain cases of dissociation with the phenomenon of *evaporation*. It has been already stated that when evaporation occurs in a confined space, it apparently ceases when as many particles leave the space and attach themselves to the surface of the liquid, as leave the surface and move about in the space, in unit time. Thus, evaporation is a reversible change capable of attaining an equilibrium stage. The number of particles of vapour which attach themselves to the surface of the liquid in unit time depends on the number which strikes the surface; according to the kinetic theory of gases, this number is measured by the pressure of the vapour, so that the evaporation ceases when the pressure of the vapour has reached a certain value. The number of particles of liquid which enter the space in unit time depends on the temperature of the liquid; the higher this is, the greater the number of particles which leave the liquid in unit time, and, therefore, the greater will have to be the number of vapour particles striking the surface of the liquid, per unit time, in order to bring about equilibrium. In other words, the higher the temperature of the liquid, the greater will be its vapour pressure when evaporation has apparently ceased.

It will be obvious from these remarks that the evaporation of a liquid is increased by raising its temperature, and is decreased by raising the pressure of its vapour above it. Thus, if the evaporation be considered as a reversible change, it is analogous to the dissociation of PCl_5 in that temperature and pressure are at war with each other in

their effect on the extent of the change. It is interesting to note that temperature eventually prevails, and that for every liquid there is a temperature above which no amount of pressure will prevent it from becoming vaporised; this is its absolute boiling-point (p. 29).

For a right understanding of the influence of pressure on evaporation (and dissociation) it is necessary to realise the principle of *partial pressure*. When two gases are mixed the resulting pressure on the sides of the containing vessel is the sum of the pressure which each gas exerted before the two were mixed; so that a *law of partial pressures* may be stated in this way: In a mixture of gases the pressure exerted by each gas is exactly the same as the pressure which that gas would exert did it alone occupy the volume filled by the mixture. Thus, in air, where the proportion of N : O is approximately 4 : 1, $\frac{1}{5}$th of the pressure is exerted by the O and $\frac{4}{5}$th by the N.

From this it follows that in a mixture of vapour and air the vapour exerts the same pressure as it would exert did it alone occupy the space filled by the mixture, and that, since the extent to which a liquid will evaporate depends, when the temperature is constant, solely on the pressure of its vapour, evaporation must proceed to the same extent in a vacuum and in air. Thus, at 15.3° C. water and its vapour are in equilibrium when the pressure of the latter is equal to 12.9 mm. of mercury, so that water will continue to evaporate until it has parted with sufficient vapour to create this pressure in the space above it. If that space originally contained a vacuum, a pressure-gauge will show a pressure of 12.9 mm. when the evaporation has apparently ceased; if the space originally contained air at 760 mm. pressure, the gauge will show a pressure of 760 + 12.9 mm.

The hastening of evaporation by a draught of air is simply due to the prevention of the accumulation of vapour over the surface of the liquid; in this way the vapour pressure may be hindered from rising to that which causes equilibrium.

From the foregoing it will be seen that the temperature and pressure of a vapour in presence of its liquid are interdependent; a given pressure of the vapour can only be attained at a certain temperature, and for a given temperature the pressure must have a certain value. In the case of unsaturated vapour and gases, pressure and temperature can be varied independently, and by an alteration of volume either temperature or pressure is varied. The sole effect of varying the volume of a vapour in presence of its liquid is to cause more liquid to become vapour, or *vice versâ*, and the temperature and pressure remain constant.

Water is one individual, capable of existing in three *phases*,* ice, water, and vapour. A system comprising water and its vapour alone, is a *two-phase* system and the phases can be in equilibrium at many different temperatures, a definite pressure corresponding with each temperature. When the pressure of the water vapour is reduced to 4.6 mm., the water passes into ice owing to the heat lost by its own evaporation, and the temperature is then 0.007° C.; any further reduction of temperature or pressure will convert all the water into ice and the system again becomes two-phase, consisting of ice and its vapour. But so long as the temperature and pressure are those named, the three-phase system—ice, water, vapour—is in equilibrium. Thus, while a two-phase system is in equilibrium under different conditions, there is only one condition of equilibrium for a three-phase system.

Water is one individual; where there are two individuals in a system, three phases may be in equilibrium at different temperatures, but when the two individuals are in four phases, only one condition of equilibrium is possible. Such a case is presented by the two individuals chlorine and water. Chlorine hydrate

* The word "phase" is applied to any constituent of a system which is capable of differentiation from the other constituents.

separates at 9.6° C. if the pressure of the chlorine is that of the atmosphere; by raising the pressure, the temperature at which the hydrate separates is raised, and a new temperature is established at each pressure; this is an interdependence similar to that in the case of evaporation, that is to say, the three-phase system Cl. $Cl.4H_2O,H_2O$ is in equilibrium at different temperatures. As soon, however, as ice begins to separate (at 0.24° C.) a fourth phase is introduced, and equilibrium between the four is only possible at this temperature, the pressure being 244 mm.

When there is only one condition of equilibrium, this is called the *transition-point*, for if the pressure or temperature be varied, one of the phases must pass into one of the others and disappear from the system.

The *phase rule*, which is believed to govern the equilibrium of heterogeneous systems, states that a transition-point for a system of n individuals is only possible when the number of phases is $n+1$.

Allotropic changes may also be brought under the phase rule. When the allotropes are *enantiotropes* (that is, when the change from one to the other is reversible, as in the case of octahedral and prismatic sulphur and red and yellow phosphorus), there is a transition-point for the phases consisting of the two forms the liquid element and the vapour.

The case of the dissociation of calcium carbonate by heat is closely analogous to that of evaporation. The reversible change, $CaCO_3 \rightleftarrows CaO + CO_2$, reaches equilibrium when the pressure of the CO_2 has attained a certain value depending on the temperature. Since the pressure of the CO_2 is a measure of the weight of it in unit volume, the equilibrium is reached when the product, CO_2, has a certain active mass dependent on the temperature. Thus, at 740° C. the equilibrium pressure is 255 mm., and when this has been attained no further dissociation can occur; if the calcium carbonate be heated in a vessel exposed to the open air, the CO_2 will gradually diffuse away and its partial pressure will be reduced below 255 mm., so that the change will continue. By exposing the heated mass to a draught of air, the admixture of the CO_2 with the surrounding atmosphere, and therefore the completion of the dissociation, will be more rapid. If the pressure of the CO_2 be not allowed to rise to 255 mm., the complete conversion of $CaCO_3$ to CaO can be effected at a correspondingly lower temperature.

A precisely similar influence is exerted by temperature and pressure on the solubility of a gas in water. The solubility decreases with rise of temperature and increases with rise of pressure. For perfect gases the following generalisation is true:—The solubility of a gas in a liquid is directly proportional to the pressure exerted by the gas. Since the volume of the gas varies inversely with the pressure, this statement may be varied thus: a given volume of liquid will always dissolve the same volume of a given gas, whatever the pressure. Thus, if a litre of water dissolve 100 c.c. of a gas at 760 mm., it will dissolve twice this quantity at 1520 mm.; but 200 c.c. measured at 760 mm. will be 100 c.c. at 1520 mm., so that the litre of water will still dissolve only 100 c.c. at the higher pressure.

Since the coefficient of solubility of a gas (p. 54) is the volume of the gas which unit volume of water will dissolve at 760 mm., it follows that the quantity of gas soluble in the same volume of water, at the same temperature, and at any other pressure, is found by multiplying the coefficient of solubility by the pressure divided by 760. In a mixture of gases the pressure of each gas is only a part of the whole, being the same fraction of the total pressure as the volume of the gas is of the total volume. The method of calculating the solubility of the N and O when air is shaken with water (p. 54) will now be easily understood, and, as a further example, the volume of CO_2 which 100 c.c. of water will dissolve from the air at 0° C. and 720 mm. may be calculated. Taking the percentage of CO_2 in the air at 0.035, its partial pressure, when the total pressure is 720 mm., will

be $\frac{0.035}{100} \times 720 = 0.25$ mm. The coefficient of solubility of CO_2 at 0° C. and 760 mm. is 1.8; therefore at 0.25 mm. and 0° C. it will be $1.8 \times \frac{0.25}{760}$. This, therefore, will be the volume of CO_2 dissolved by 1 vol. of water under the conditions named; when multiplied by 100, the value will express the number of c.c. dissolved by 100 c.c of water.

It must be remarked that gases which are easily liquefied, and thus deviate from true gases, fail to obey with accuracy the law of solubility stated above.

When the space above the solution of a gas contains the same gas as that which is dissolved, equilibrium is established when the same quantity of gas passes from the space into the liquid, and from the liquid into the space, in unit time. If for the gas in this space there be substituted another, the dissolved gas will go on escaping from solution until its partial pressure in the space is the same as its pressure was when it alone filled the space. It will be obvious, therefore, that a few such displacements of the gas in the space should cause the liquid to part with practically all its dissolved gas.

Solution.—In the case of most gases it is impossible to regard their solutions in water as mere physical mixtures. Reference has been already made to this difficulty and to the companion one concerning the solubility of solids (p. 50). Besides the thermal changes there mentioned, there are such facts as the constant boiling-point of solutions containing gas and water in definite proportions—*e.g.*, $HCl.8H_2O$ (p. 179), and the separation of salts containing water of crystallisation—to compel the conclusion that in many cases the dissolved substance enters into combination with the solvent.

It is a fact, however, that many dilute solutions behave as would be anticipated if the dissolved substance were present in a condition independent of the solvent. Thus, it has been discovered that the molecules of a dissolved substance exert a pressure on the solvent identical with the pressure which they would exert on the sides of a vessel, of the same volume as that of the solution, if they were in the gaseous state.

This discovery has given rise to a "physical theory" of dilute solutions, which may be stated thus: The molecules of the dissolved substance pervade the solvent without being influenced thereby, and possess the same properties as they would possess did they alone, in the state of gas, occupy the volume filled by the solution.

The pressure which a substance in solution exerts on the solvent is called the *osmotic pressure* of the solution, because it is only by taking advantage of the phenomenon of osmosis that it can be rendered apparent and directly measured. It has been already shown (pp. 70, 277) that certain structureless substances (india-rubber, parchment paper, &c.) will allow of a much more rapid passage through them of some kinds of molecules than of other kinds. Several such substances exist which allow water molecules to pass through them almost infinitely faster than they allow many other kinds of molecules to pass. When a membrane made of one of these substances is immersed in an aqueous solution, it will generally happen that the water molecules will pass through the membrane very much faster than the molecules of the dissolved substance. This transition of molecules differs from that called diffusion, in that it appears to depend rather upon the specific nature of the membrane than upon its porosity (compare p. 22). The term *osmosis* is introduced to indicate this difference.

The method employed for studying the pressure exerted by a dissolved substance on the solvent, can now be easily understood. A vessel is

constructed of a material which allows of the osmosis of the solvent molecules, but not of the dissolved molecules. The solution whose osmotic pressure is to be studied, is introduced into this vessel, which is then immersed in a bath of the pure solvent. The solvent molecules will pass into the vessel and out of the vessel; but since there are more of these molecules in unit volume outside the vessel than there are inside (on account of the presence of the dissolved molecules), more of the solvent will pass into the vessel in unit time than will pass out, and equilibrium will only be established when a certain pressure, compensating for this difference between the number of solvent molecules in unit volume, has been established inside the vessel. This pressure is termed the osmotic pressure of the solution, and is attributed to the dissolved molecules; it can be measured by closing the vessel by an ordinary pressure-gauge.

In practice it is found necessary to support the "osmotic membrane" which is to form the walls of the vessel, by depositing it on the surface of a porous pot. The most successful method consists in depositing copper ferrocyanide (a material which behaves as an osmotic membrane to aqueous solutions) within the pores of a biscuit-porcelain battery cell (3″ × 1″); for this purpose the cell is filled with a solution of copper sulphate (3 per cent.) and immersed in a solution of potassium ferrocyanide (3 per cent.). The two solutions meet in the wall of the cell, and a continuous sheet of copper ferrocyanide is deposited therein. An inverted funnel is cemented in the mouth of the cell, and a U-shaped mercury gauge is sealed to the stem of the funnel. The cell is nearly filled with the aqueous solution whose osmotic pressure is to be measured, and is immersed in a bath of distilled water. The pressure of the air trapped between the gauge and the solution is measured by the variation in the height of the mercury in the gauge.*

It is found that the same relationship exists between the osmotic pressure and the concentration of a solution as exists between the pressure and the concentration of a gas. That is to say, the osmotic pressure is directly proportional to the weight of dissolved substance in unit volume of the solution, just as the pressure of a gas is directly proportional to the weight of the gas in unit volume (Boyle's law). Thus, a one per cent. sugar solution exerts an osmotic pressure equal to 535 mm. of mercury, whilst the osmotic pressure of a two per cent. solution is equal to 1070 mm., provided the temperature is the same in each case.

Again, the osmotic pressure of a solution varies directly as the absolute temperature (thermometric temperature + 273) of the solution, just as the pressure of a gas varies directly with its absolute temperature (Charles' law). Thus the one per cent. solution of sugar shows an osmotic pressure of 544 mm. of mercury at 32° C., and of 512 mm. at 14.15° (305 : 287.15 = 544 : 512).

It seems, then, that the variations which occur in the osmotic pressure of a dilute solution when the concentration of the solution is varied, are controlled by the same laws as those which govern the variations in the pressure of a gas when the concentration of the gas is varied. But the analogy between the osmotic pressure and the gaseous pressure is still closer than this; for it is found that *the osmotic pressure is identical with the gaseous pressure which the weight of dissolved substance would*

* A description and drawing of the apparatus will be found in *Jour. Chem. Soc. Trans.* 1891, p. 344, and directions for preparing the membrane by electrolysis are given in the *Amer. Chem. Jour.*, 1901, vol. 26, p. 80.

exert at the same temperature, if it were in the state of gas and occupied the volume filled by the solution.

It is considered reasonable to deduce from this that the number of molecules of dissolved substance in a volume v of a solution, having an osmotic pressure p and a temperature t, is the same as the number of molecules in a volume v of a gas at the pressure p and the temperature t.

Thus, a 1 per cent. solution of cane sugar ($C_{12}H_{22}O_{11}$) at 0° C. exerts an osmotic pressure of 493 mm. Now the molecular weight corresponding with the formula $C_{12}H_{22}O_{11}$ is 342, and, could the sugar be gasified, 342 grams of it would occupy 22.22 litres at 0° C. and 760 mm. (p. 47); that is to say, 342 grams of gaseous sugar in a volume of 22.22 litres at 0° C. would exert a pressure of 760 mm. The concentration of 342 grams in 22.22 litres is the same as a concentration of 15.4 grams in one litre; therefore 15.4 grams of gaseous sugar in 1 litre at 0° C. should exert a pressure of 760 mm. It follows that 10 grams in 1 litre at 0° C. should exert a pressure of 493 mm. This is practically identical with the osmotic pressure of a (1 per cent.) sugar solution containing 10 grams per litre.

Gases at high concentration—that is, at high pressure—cease to obey the laws of Boyle and Charles. The same is true for solutions at high concentration.

Since Avogadro's law is deducible mathematically from those of Boyle and Charles, and since dilute solutions appear to be controlled by the last-named laws, it seemed probable that an Avogadro's law should exist for dilute solutions. This was first pointed out by Van't Hoff, whose *law of osmotic pressure* is thus stated: Equal volumes of different solutions, at the same temperature and osmotic pressure, contain equal numbers of molecules of dissolved substance.

The similarity between this statement and that expressing Avogadro's law (p. 289) will be at once evident.

Solutions which exert equal osmotic pressure are said to be *isotonic*.

Just as the relation between the weights of the molecules of two gases can be deduced from Avogadro's law (p. 289), so can the relation between the weights of the molecules of two dissolved solids be deduced from Van't Hoff's law. For it follows from this law, that when equal volumes of two solutions are isotonic, and at the same temperature, the weight of dissolved solid in the one is as much heavier than the weight of the dissolved solid in the other, as the molecular weight of the first solid is heavier than the molecular weight of the second (*cf.* footnote, p. 47).

Determination of molecular weights of non-volatile substances.—The applicability of the measurement of osmotic pressure to the determination of molecular weights will now be easily understood. A solution of the solid whose molecular weight is unknown may be diluted, or strengthened, until its osmotic pressure is identical with that of a solution containing a known weight of a solid whose molecular weight is known. The ratio between the weights of the solids in one litre of each solution is then the ratio between the molecular weights of the solids.

Example.—A solution of a substance of unknown molecular weight was diluted until its osmotic pressure was found to be identical with that of a solution of sugar in water (at the same temperature). The weight of solid in 1 litre of each solution was then determined; that in the sugar solution was 1 gram; that in the other solution was 1.5 gram. By Van't Hoff's law these weights must have the same ratio to each other as have the molecular weights of the substances. Let x be the unknown mol. wt.; the mol. wt. of sugar is 342, therefore:

$$342 : x :: 1 : 1.5 \text{ or } x = 342 \times 1.5.$$

The measurement of osmotic pressure is neither easy nor capable of

very great accuracy; it is not, therefore, well adapted for the determination of molecular weights.

There are, however, other methods of determining whether solutions contain the same number of dissolved molecules in equal volumes, which, owing to the ease and accuracy of making the required measurements, are much adopted for checking, and even determining, the molecular weights of substances which cannot be volatilised, and are therefore excluded from the method depending on the determination of the vapour density of the substance (p. 292).

The methods in question depend upon the influence which the molecules of the dissolved substance have on many of the physical properties of the solvent. Thus, the more numerous the dissolved molecules in a solution the lower will be its freezing-point and its vapour pressure, so that a measurement of the temperature at which the solution freezes, or of the pressure exerted by its vapour, will serve as a measurement of the molecular concentration of the substance in solution.

The method of determining molecular weights which depends upon the measurement of the freezing-point of a solution is known as the *cryoscopic method*, or the *method of depression of the freezing-point*, as *Raoult's method*.

Raoult discovered, empirically, that the freezing-point of a solution is always lower than that of the solvent, and that the depression is directly proportional to the weight of substance in solution. Thus, if one gram of a solid in a litre of water lowers the freezing-point by 0.1°, two grams will lower it 0.2°. Collation of his results showed that *when molecular quantities of different substances are dissolved in the same amount of a solvent, they lower the freezing-point of the solvent to the same extent.* This may now be expressed by saying that isotonic solutions in the same solvent have the same freezing-point.

If Raoult's generalisation (italicised above) be true, there will be a certain constant (T) for every solvent, representing the amount of depression in the freezing-point of that solvent caused by the presence of one gram-molecule of any substance in 100 grams of the solvent. Thus, it is found that in the case of many salts, a solution of one gram-molecule of the salt in 1000 grams of water freezes at $-1.9°$ C.; consequently a solution of one gram-molecule in 100 grams of water should freeze at $-19°$ C., and the constant, T, for water is 19. This value does not hold good for all classes of salts for a reason to be explained later.

A little consideration will show that when T is known for a solvent, it should be possible to determine the molecular weight of a substance by ascertaining the depression of the freezing point of a solution of the substance in that solvent.

Suppose the constant T to have been ascertained for a solvent. This would be effected by determining what depression is caused in the freezing-point of the solvent by dissolving 1 gram-molecule of any substance of well-known molecular weight in 100 grams of it. Let it be desired to determine the molecular weight (M) of some other substance. One gram of the substance is dissolved in 100 grams of the solvent, and the freezing-point of the solution is determined; suppose this to be k degrees lower than the freezing-point of the pure solvent. Then, if one gram cause depression k, M grams (one gram-molecule) will cause depression Mk; but this depression is the value T, whence, $Mk = T$ or $M = T/k$. Since T and k are known, M is thus determined.

The depression caused by one gram in 100 grams of solvent is generally too small to measure, so a stronger solution, say P grams in 100 grams of solvent, is used.

If P grams cause depression k, one gram will cause depression k/P, and M grams will cause depression Mk/P. Therefore $Mk/P = T$ or $M = TP/k$.

The value of T for water is 19 for several classes of salts; for benzene it is 49 for glacial acetic acid it is 39.

The method is conducted as follows: A known weight of the solvent is introduced into a long test-tube (Fig. 202) which has a side neck closed by a cork; a cork in the mouth of the test-tube carries a thermometer, graduated to 0.01°, and a stirrer. The test-tube is passed through the cork of a wider test-tube (to serve as an air jacket, which shall prevent too rapid a change of temperature), which is immersed in a bath also provided with a stirrer and at a temperature several degrees below the freezing-point of the solvent. The bulb of the thermometer being immersed in the solvent, the stirrer is continually agitated until the solvent begins to freeze, whereupon the temperature is noted. The tube is then withdrawn from the bath, the solvent allowed to melt, and the weighed quantity of substance added through the side neck. When this has dissolved, the freezing-point of the solution is determined as before. Since superfusion of the solution is liable to occur it is sometimes necessary to add a crystal of a previously frozen solution (of the same strength) in order to induce solidification.

Fig. 202.—Beckmann's apparatus.

Example.—The freezing-point of 120 grams of benzene was found to be 6° C.; 6 grams of sulphur were dissolved in the benzene and the freezing-point was again determined; it was found to be 4.68° C. In this case 120 grams of benzene contained 6 grams of sulphur, so that P, the quantity present in 100 grams, is $\frac{100}{120} \times 6 = 5$ grams. $k = 6 - 4.68 = 1.32$. T for benzene = 49. Therefore $M = \frac{46 \times 5}{1.32} = 185.6$. Thus the molecular weight of solid sulphur is 185.6, a number sufficiently close to 192 to warrant the conclusion that the molecule of solid sulphur is S_6.*

The *lowering of the vapour pressure* of a solvent by the presence of a substance in solution, is controlled by laws which are wholly similar to those which apply to the lowering of the freezing-point of a solvent by the presence of a dissolved substance. Since the vapour pressure varies with the temperature, it is necessary to add that the lowering is always the same fraction of the vapour pressure of the pure solvent, whatever the temperature.

Inasmuch as the boiling-point of a liquid is that temperature at which the pressure of its vapour is equal to the pressure of the atmosphere, the presence of a dissolved substance must raise the boiling-point of a solution *pari passu* with lowering its vapour pressure.

The apparatus shown in Fig. 203 is used for determining the rise of the boiling-point of a solvent by the presence of a dissolved substance. To avoid heating the solvent to a temperature above its boiling-point, which would vitiate the result, the tube containing the solvent is surrounded by a jacket filled with an atmosphere of the vapour of the solvent at its boiling-point. This vapour is generated in the flask A and is passed through the tube B, provided with distributing holes at its lower end, into the inner tube N which contains another portion of the solvent. When

* Determinations of the vapour pressure of CS_2 when sulphur is dissolved in it, show a value of S_3 for the molecule of solid sulphur.

the latter has been heated by the vapour to its boiling-point, the vapour passes uncondensed through the solvent and through the hole H, thus surrounding the tube N and passing into the condenser C. The temperature is now noted by the thermometer T, the tube N is emptied and the operation repeated with the addition to the solvent (about 5 to 7 c.c.) of a weighed quantity of the substance (about 4 per cent. of the weight of the solvent), the molecular weight of which is to be determined. The tube N, whose weight when empty is known, is now weighed to ascertain the weight of solvent used. The molecular elevation of the solvent having been determined by the use of a substance of known molecular weight, the molecular weight of the substance is calculated as in the freezing-point method described above.

Fig. 203.—Landsberger's apparatus.

It must here be noted that there are many cases in which the molecular weight of a compound, determined by the osmotic pressure of a solution of it, or by the cryoscopic method, is only a fraction of the molecular weight which must be assigned to the substance on account of the other considerations which serve to settle molecular weights. A flagrant case is that of potassium chloride. The osmotic pressure of a dilute aqueous solution of this salt is nearly twice as great as it should be if the molecular weight of the salt be 74.5; again, the depression of the freezing-point of a dilute solution is nearly twice as great as it should be if the molecular weight of the salt were 74.5. Both these facts indicate that potassium chloride, in solution, has a molecular weight

about one half of 74.5, and yet a quantitative analysis of KCl shows that 74.5 parts by weight of it contain 35.5 parts by weight of chlorine, so that the salt cannot well have a smaller molecular weight than 74.5. This anomalous behaviour of KCl is shared by a large number of salts, acids and bases, all of which show a lower molecular weight when in solution than that which is generally attributed to them.

This phenomenon is so analogous to that of the dissociation of a compound (*e.g.*, NH_4Cl, PCl_5) by heat, which causes the molecular weight determined by the vapour density to be lower than that inferred from other considerations, that these salts, acids and bases are supposed to have been more or less dissociated by the water which has dissolved them. Thus, potassium chloride—which gives an osmotic pressure nearly twice that which it should give if its molecule, in dilute solution, were represented by KCl—is supposed to be nearly completely dissociated into K and Cl; so that there are twice as many ultimate particles in the solution as there would be if the dissociation did not occur—just as there are twice as many molecules, causing twice as great a pressure, in the vapour of PCl_5 above 300° C. as there would be if no dissociation occurred.

The realisation of the existence of osmotic pressure renders it possible to regard the process of dissolution of a solid as belonging to the same type of changes as that to which dissociation and evaporation have been assigned. When a salt is immersed in water particles of salt leave the mass and pervade the water, this process continuing until as many particles leave the mass of salt as attach themselves to it, in unit time. This equilibrium stage is the saturation of the water with the salt, and for every temperature there is an appropriate pressure—the osmotic pressure—at which equilibrium will occur, just as there is an appropriate vapour pressure for every temperature at which evaporation will cease.

Electrolysis.—The theory that many molecules are dissociated by being dissolved, finds its chief support in a study of the phenomena which accompany the conversion of chemical energy into electrical energy and *vice versâ*.

The chemical action which is most frequently employed to develop chemical energy for conversion into electrical energy, is that involved in the dissolution of zinc in an acid, generally dilute sulphuric acid. If a piece of commercial zinc be immersed in dilute sulphuric acid, it dissolves, and a quantity of heat is developed equivalent to the chemical energy of the dissolution of the zinc. If the zinc and acid be perfectly pure no action will occur; but if a piece of platinum be immersed in the acid and be made to touch the zinc, whether beneath or above the surface of the acid, action will begin and heat will be developed; the hydrogen will no longer appear to be evolved from the zinc, but will rise from the surface of the platinum. In the case of both the impure zinc and the zinc + platinum, the chemical energy has to a great extent passed through the stage of electrical energy before it has become heat energy.*

If the platinum and zinc be connected with a wire outside the acid,

* The impure zinc contains foreign metals which, by contact with the zinc, enable the latter to dissolve, with generation of electrical energy, just as the platinum enables the pure zinc to dissolve.

the electrical energy will "flow" through the wire and may be utilised before it becomes converted into heat energy.

When such a "galvanic cell" is left to itself, the rapidity of the dissolution of the zinc soon diminishes (and with it the intensity of the electrical energy) because the cell becomes *polarised;* this is chiefly due to the coating of the platinum plate with hydrogen so that it virtually becomes a plate of hydrogen, which is much less effective than is platinum in aiding the dissolution of zinc by contact. It is for this reason that all cells which have any practical value contain an oxidising agent or *depolariser* (*e.g.*, nitric acid in a Grove cell) around the platinum plate; such an agent, by oxidising the hydrogen, diminishes the polarisation, and at the same time develops a greater amount of chemical energy, and therefore of electrical energy, in the cell.

The total amount of electrical energy developed by a galvanic cell in unit time, depends on the amount of chemical energy occurring in the cell in that time, and upon the nature of the plates which are used in the cell. The first of these conditions is measured (in the zinc cell) by the amount of zinc which dissolves, and is therefore related to the size of the zinc plate.* The influence of the nature of the plates may be summed up by saying that the greater the antithesis between the plates, in respect of the ease with which they are attacked by the exciting medium of the cell, the greater will be the total amount of electrical energy obtained from the cell. Thus, when dilute sulphuric acid is the exciting medium, the plates should consist of a metal which is, in a high degree, attackable by this acid, and one which is highly resistant; zinc and platinum are the metals, among those which are sufficiently cheap for use, which best fulfil these conditions; zinc and copper are frequently used, but since copper has a greater tendency to dissolve in sulphuric acid than platinum has, this "couple" is not capable of giving so great a total of electrical energy as that yielded by a zinc-platinum couple. It will be obvious, however, that in the event of an exciting medium which has more action on platinum than on copper being used, the zinc-copper couple may transcend the zinc-platinum couple.

Since it is a *sine quâ non* that the plates used in a battery should be conductors of electricity, the non-metals with a few exceptions (the most notable of which is carbon) are put out of court for this purpose.

It is necessary to add that the total amount of electrical energy is made up of two factors; one of these is analogous to the factor expressed by the specific heat of the hot body, in heat energy, and is generally called *intensity of current;* whilst the other is analogous to the temperature of heat energy, and is generally called *electromotive force* or *pressure.* It is the second factor, the pressure, which varies with the nature of the plates. The first factor is dependent upon the amount of chemical action, just as the number of units of heat evolved in a chemical reaction is dependent upon the amount of chemical action.

The word *electrolysis* is used to signify the decomposition of a compound by the passage through it, or its solution, of the electric current. Any compound which can be thus decomposed is termed an *electrolyte*, and the portions into which it is decomposed are termed *ions*. An electrolyte must be a compound, but all compounds are not electrolytes. Compounds may be classified with regard to their relation to the electric current into (1) conductors which are not electrolytes, (2) conductors which are electrolytes, and (3) non-conductors.

Electrolysis is effected by passing the current through the electrolyte, most conveniently from two plates, made of some conductors and called electrodes. The plate connected with the less attacked metal of the battery (*e.g.*, Pt.) is regarded as the one by which the electric current enters the electrolyte, and is called the *anode* or the *positive* electrode. The other plate, attached to the more attacked plate of the battery, is

* If the zinc plate be badly amalgamated (p. 14) the impurities in it will develop minor electric currents, causing evolution of hydrogen "from the zinc," and the amount of electrical energy thus developed will be unavailable for external use, and will be directly converted into heat.

supposed to afford an exit for the current, and is called the *cathode* or the *negative* electrode.

The electrolyte is always split up into two chemically equivalent ions; these are either liberated at the electrodes, or there enter into reaction with the electrolytic medium, as will be explained below. Ions which are liberated at the anode are *anions*, whilst those liberated at the cathode are *cations*. Since unlike electricities attract each other, and the anode is supposed to contain positive electricity, the anions are electro-negative elements or radicles; the cations are the electro-positive elements or radicles (p. 15). Attempts are made to catalogue the elements in the order of their decreasing electro-positiveness; that is, in such an order, that if a compound of any two elements be submitted to electrolysis, the one which comes first in the list will behave as the cation. It is obvious that such an *electro-chemical* list must differ according to the conditions of the electrolysis (such as whether the compound be present in an acid or an alkaline electrolytic medium, &c.).

In nearly all cases, however, the metals precede the non-metals in these lists, and when the list is drawn up with reference to electrolysis in neutral or acid solution, the metals follow each other in the order of their affinity for oxygen. From what was stated with regard to the use of metals as battery plates, it will be obvious that that metal which has least affinity for oxygen, and is, therefore, least readily attacked by acids, will generally be best suited for the resistant plate in a cell.

The ions of an electrolyte are either atoms or radicles; thus, when an aqueous solution of HCl is electrolysed, the ions are H and Cl, these being chemically equivalent; the H atoms move towards the cathode, each carrying its charge of positive electricity, the Cl atoms move towards the anode, each carrying its negative charge. In the case of an aqueous solution of K_2SO_4, the ions are K_2 and SO_4, these being chemically equivalent; each K atom carries one positive charge, whilst the SO_4 radical carries two negative charges. When the ions reach the electrodes the charges (*electrons*) are neutralised, and the ions either appear in the free state (when the atoms immediately combine to form molecules), or they react with the water or with the electrode; in the latter case the final products of the electrolysis will be the products of these reactions. In the case of hydrochloric acid electrolysed by carbon electrodes, molecules of hydrogen and chlorine are evolved. In the case of potassium sulphate electrolysed with carbon or platinum electrodes, the final products are hydrogen at the cathode and oxygen at the anode; for the potassium atoms, so soon as they are discharged at the cathode, react with the water in the well-known manner producing $2KOH$ and H_2, whilst the SO_4, when it is discharged, reacts with the water, producing H_2SO_4 and O. The $2KOH$ and H_2SO_4 left in solution speedily neutralise each other, re-forming potassium sulphate, the total quantity of which thus suffers no diminution during the electrolysis.

It will now be realised that the electrolysis of water described on p. 13 is the electrolysis of dilute sulphuric acid. Water, so far as is known, is not an electrolyte; when dilute sulphuric acid is electrolysed, hydrogen is liberated at the cathode and SO_4 at the anode, where it at once reacts with the water to form H_2SO_4 and O.

When copper sulphate solution is electrolysed with platinum elec-

trodes, the ions are Cu″ and SO_4. The copper is deposited on the cathode and oxygen is evolved at the anode, owing to the reaction between discharged SO_4 and water. If the anode be made of some material which is more easily attacked by SO_4 than is water, this will react with SO_4. Thus, a copper anode will be dissolved by combining with the SO_4, and the quantity of copper which will pass into solution will be exactly equal to that deposited on the cathode; this fact is applied in the process of electro-plating (*see* Silver).

Faraday's *law of electrolysis* states that the same intensity of electric current will liberate all ions in the proportion of their chemical equivalents. For example, if the same current of electricity be passed through electrolytic cells containing sulphuric acid and silver nitrate respectively, there will be 108 grams of silver deposited on the cathode of the one cell for every 1 gram of hydrogen liberated at the cathode of the other cell, these quantities of silver and hydrogen being chemically equivalent. So also there will be 48 grams of SO_4 discharged at the anode of the one cell, and 62 grams of NO_3 at the anode of the other cell.

Since some elements have two chemical equivalents, ions composed of them will have two *electro-chemical equivalents*. Thus, copper in cupric chloride has an electro-chemical equivalent of 31.5, this proportion being deposited for every 1 part of hydrogen evolved in a sulphuric acid cell; but copper in cuprous chloride has an electro-chemical equivalent of 63.

The converse of Faraday's law is equally true; that is to say, the chemical change of chemically equivalent quantities of ions gives rise to the same intensity of electric current. Thus, in a galvanic cell the same intensity of current will be generated, whether 32.5 parts of zinc or 28 parts of iron be dissolved in acid.

The intensity of electric current necessary to decompose 1 gram-equivalent of any electrolyte is 96,540 units (*coulombs*). But this is only one factor of the electrical energy required, for the latter is the product of the intensity of current × the pressure at which it is delivered. The pressure necessary for electrolysing any particular electrolyte depends on the chemical affinity of the ions for each other. If now the heat equivalent to this chemical affinity be known, the electrical energy can be calculated, because 1 unit of electrical energy (*joule*) is equal to 0.24 gram-unit of heat. The joule = 1 coulomb × 1 volt (the unit of pressure). Let a be the heat equivalent to the affinity between 1 gram equivalent of each of the ions; this will be equal to $a/0.24$ joules. But the intensity of current necessary to effect the electrolysis is 96,540 coulombs, so that the electrical energy must be made up of 96,540 coulombs × x volts; thus the equation $a/0.24 = 96540 \times x$ is obtained, from which the value of x, the voltage necessary for the electrolysis, may be calculated. The value ascertained in this manner is, of course, open to the same uncertainty as that which surrounds the value for the heat equivalent to the affinity (p. 308).

The best electrolytes are aqueous solutions of powerful acids and bases, and of salts. Feeble acids are poor electrolytes. Fused salts are generally electrolytes. It is necessary to refer to the question as to what constitutes an electrolyte.

It is generally stated that the transmission of the electrical energy, commonly called the electric current, can occur in two ways, either along matter or with matter. The first method of transference happens when electricity is conducted by a metal; substances which are able to effect such a transference are called conductors of the first class. The second

method is that which obtains in electrolytes, which are called conductors of the second class.

These facts were early recognised, but it was at first thought that the electricity obtained the matter with which it was to move in the electrolyte by tearing asunder the molecules. This, however, would be inconsistent with the fact that even the smallest electrical pressure will exert some electrolysis. It has only recently been realised that the molecules in an electrolyte must be regarded as being already *ionised*, nearly completely in dilute solutions, and to a certain extent in all electrolytes. The free ions exist in the electrolytic medium, each bearing its charge of electricity. It is this charge that prevents the ion from behaving chemically like the free element or radicle, and it is only when the ion has been conducted to the electrode by the electric current, and is discharged, that it exhibits the chemical properties expected of the free element or radicle.

That this view of the constitution of an electrolyte is correct is evidenced by the facts concerning the conductivity of saline solutions. If the passage of an electric current through an electrolyte depends upon the presence of ions, a saline solution should offer a lower resistance to this passage the more perfect the ionisation of the dissolved salt. Hence the conductivity of a dilute solution, in which ionisation is more perfect, should be proportionally better than that of one which is stronger, and therefore less ionised. This is found to be the case; as the dilution of a saline solution is increased the conductivity tends to become constant, the more perfect ionisation compensating for the smaller number of ultimate particles in unit volume.

Judging by conductivity, ionisation appears to be practically complete when one gram-equivalent of a salt is dissolved in 1000 litres of water; the degree of ionisation at any other dilution is equal to the ratio of the molecular conductivity (the conductivity calculated, from the observed value, for a solution containing 1 gram-molecule per litre) at this dilution to the molecular conductivity at a dilution of 1000 litres. This statement only applies to good electrolytes; poor electrolytes do not reach a constant conductivity at any dilution at which it is practicable to make the necessary measurements.

The degree of ionisation may also be calculated from measurements of osmotic pressure, for this is proportional to the ionisation. If N be the number of ultimate particles present when the osmotic pressure is P, and N^1 the number when it is P^1, then $P : P^1 = N : N^1$. The number of ultimate particles present at any degree of ionisation depends on the nature of the dissolved substance: for this may split up into n ions; in the case of H_2SO_4, $n = 3$; in the case of K_4FeCy_6, $n = 5$. If ionisation were complete, the original number of molecules, N, would become nN. Let x be the fraction of the total number of molecules ionised, then $1 - x$ will be the fraction left unionised. The total number of unionised molecules will be $N(1 - x)$, and Nx will be ionised. But Nx molecules become nNx ions, so that the total number of ultimate particles in the ionised solution will be $N(1 - x) + nNx$, and this is the value of N^1 in the above equation. Therefore $P : P^1 = N : N(1 - x) + nNx$. Whence $x = \frac{P^1 - P}{P(n-1)}$.

It is found in many cases that during electrolysis the concentration of the electrolyte at the anode (or cathode) becomes greater than that at the cathode (or anode). This can only be explained by assuming that the anions (or cations) move faster through the liquid than the cations (or anions) do. This difference in the rate of *migration* of the ions is also indicated by the fact that the conductivity of solutions containing equivalent quantities of various salts which are ionised in the same degree, is different. When a solution of KCl is electrolysed, the concentration at the electrodes remains practically the same, so that the ions of K and Cl move at nearly the same rate; but the equivalent conductivity of NaCl solution of equiva-

lent strength is only about 65 per cent. of that of KCl solution; hence the sodium ion must migrate at only 65 per cent. of the speed of the potassium ion.

It is supposed that those solutions which are not electrolytes contain no ionised molecules; thus, sugar, a solution of which is not an electrolyte, does not suffer ionisation when dissolved.

The solutions of all substances which are electrolytes show abnormal osmotic pressures, abnormal depressions of the freezing-point, &c.; this supports the theory that many salts, acids and bases are dissociated when they are dissolved. It must be remembered, however, that the dissociation is always into ions, and not necessarily of the same character as the dissociation effected by heat.

At the present day the theory of ionisation is being extensively adopted as affording the best explanation of chemical reactions in solution. The analytical tests for metals and acid radicles are the reactions of the ions; if a reaction occurs in a dilute solution which will not occur in a strong one it is because there are no ions in the strong solution, the salt not having been ionised therein.

From what has been said above on the physical theory of solution and the evidence in support of it, it will be seen that a solvent has an effect upon a soluble substance which may be well compared with the effect of heat on a volatile substance. Just as there are many substances which resist in a high degree the disgregating action of heat, so there are many which resist that of solvents. Equally noteworthy is the similarity which exists between the influence of solvents and of heat on chemical change: reactions occur between substances in solution which have no tendency to happen between the solid substances, however finely these may be divided, and however intimately they may be mixed; so also, reactions occur at an elevated temperature which are impossible at low temperatures. It is also worth while to call attention to the fact that the presence of the best solvent, water, will enable a smaller stress to convert the potential energy of a mixture into the kinetic energy represented by the combination of its constituents than would otherwise be the case; thus, as has been already stated, a mixture of carbon monoxide and oxygen requires a far greater stress in the form of high-pressure heat (high temperature) to start combination, when it is perfectly dry than when moisture is present. Many cases have been cited in which the presence of water enables a chemical change to be brought about by heat of moderate temperature—*e.g.*, the combustion of carbon (p. 32); there is not sufficient evidence to show whether or not the stress of a much higher temperature will render these changes, also, independent of moisture.

There are, however, many changes, which are capable of occurring at the ordinary temperature, that are dependent on the presence of water. It is also a fact that many substances which are excellent electrolytes when dissolved in water, have an almost infinite electrical resistance when anhydrous; in other words, these substances require the presence of water in order that they may become partially ionised. On the basis of this latter observation it has been suggested that an electrolytic medium, that is, one which will enable ionisation to occur, is essential for chemical change; on this hypothesis the fact that anhydrous HCl will not attack calcium oxide, would be explained by stating that it is only the ions of HCl which can enter into reaction with CaO. A very little water should suffice for the reaction, since when the first formed ions have been removed by reaction with the CaO, further ionisation could occur. The discovery of some other third substance which shall have a similar influence to that of water is the present business of the chemist.*

As a final word on this subject, attention must be called to the fact that high heat pressure and high electrical pressure are not alone in inducing chemical

* A tendency to return to the old view that chemical energy is to be regarded as due to a difference of electrical potential between elements, seems at present prevalent, and it must be admitted that support for such a view is derived from the recent observations of Baker, who shows that when electrodes, carrying high pressure electricity, are introduced into a mixture of hydrogen and oxygen, sufficiently dry to hinder combination, the gas around the "positive" electrode is richer in oxygen than that around the opposite electrode.

change; it has been shown that high mechanical pressure is in many cases effective (such as in decomposing moist silver chloride), and the influence of another form of energy, the shorter wave lengths of light, in inducing the numerous changes on which the art of photography depends, is well known.

Spectroscopy.—Heated solids have their molecules vibrating in so many phases that they give rise to waves in the luminiferous ether which are of every possible wave length; consequently a heated solid gives a continuous spectrum in which the red is more prominent at lower temperatures. Heated gases, on the other hand, have their molecules vibrating in such a way that they give out waves of comparatively few wave lengths.

By passing the light emitted from a hot gas through a prism the wave lengths are separated and take up their proper positions in the spectrum—*i.e.*, somewhere in the violet, indigo, blue, green, yellow,

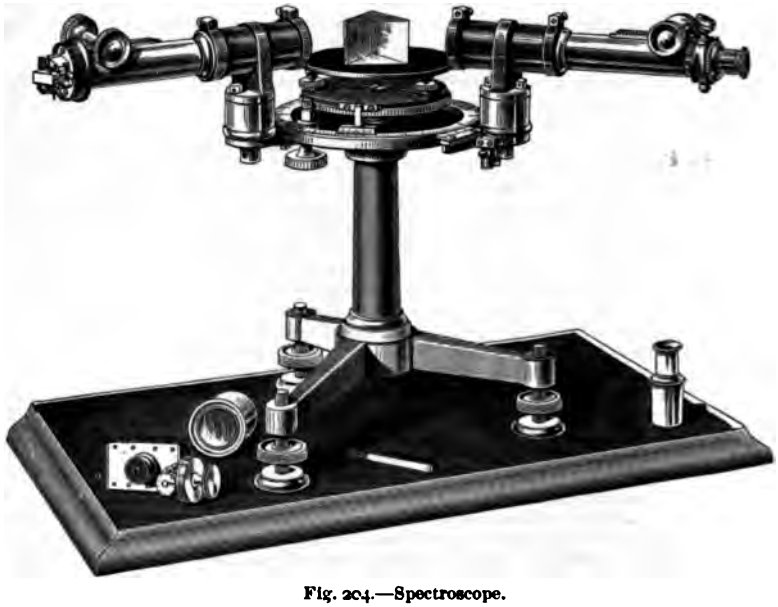


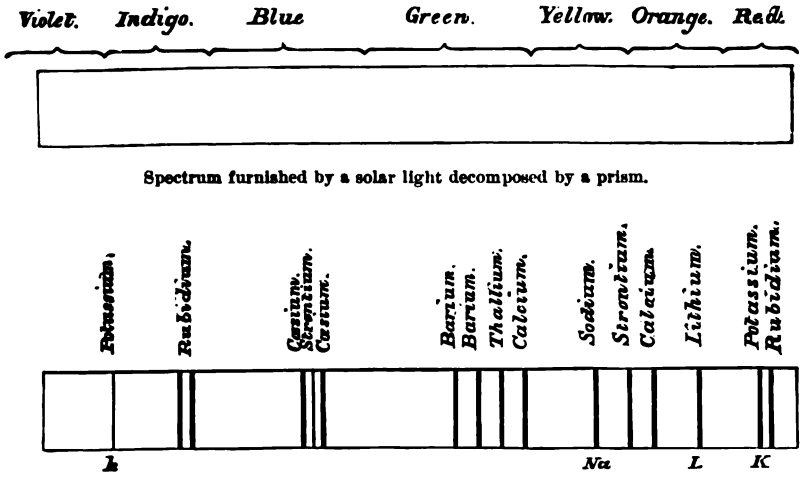
Fig. 204.—Spectroscope.

orange, red—in accordance with the length of the wave between the limits 766 millionths of a millimetre for red, and 396 millionths of a millimetre for violet. Of all the wave lengths from a given gas a few will be more visible than the rest; so that there are characteristic lines in the spectrum for the gas of each element. Thus, heated sodium vapour gives rise to two very prominent wave lengths (589.5 and 588.9 millionths of a millimetre) which give the sensation of yellow light.

When the white light emanating from an ordinary flame is allowed to pass through the narrow slit, or collimator, of a *spectroscope* (Fig. 204),*

* This form of instrument has been found to be well suited to the general work required of a spectroscope in a chemical laboratory. Either one or two prisms can be used, and the central table is arranged so as to take the levelling screws of a reflection grating. The instrument is well adapted for determination of refractive indices and dispersive powers.

and is transmitted through a prism of flint glass, a continuous spectrum composed of overlapping images of the slit in all the colours which make up white light will be perceived through the telescope; but if a Bunsen flame be employed, a single image will be seen, forming a bright yellow line in the place where the brightest yellow was seen in the continuous spectrum; this line is due to the presence of a little sodium in the flame, from the dust in the air, and it becomes very intense if a little sodium chloride be held in the flame on a loop of platinum wire. By comparing the spectra of the flames containing vapours of the metals with a map of the wave lengths in the solar spectrum (Fig. 205), the exact position of the various colours may be noted, and thus, if several metals are present in the same flame, they may still be distinguished by the colours and positions of their bright lines. Thus, if a mixture of the chlorides of potassium, sodium, and lithium be taken upon a loop of



Spectrum furnished by a solar light decomposed by a prism.

Coloured bands in the spectrum.

Fig. 205.

platinum wire and held in the flame, the dull red line of potassium (K, Fig. 205) is seen close to one end of the spectrum; at some distance from it the bright red band (L) of lithium; at about the same distance from this, the pale yellow lithium line; and close to this the bright yellow sodium lines (Na); whilst near the other end of the spectrum is the feeble violet line of potassium (*k*). The chlorides of the metals are most suitable for this experiment on account of their volatility. Since a very little vapour (for instance, $\frac{1}{100000}$ mgm.) can be detected by its characteristic wave lengths, the use of the spectroscope furnishes an extremely delicate test for many elements.

The character of the spectrum of a gas differs with the temperature and pressure. Increased temperature increases its complexity, the bright lines becoming more numerous and broader. The same effect is produced by increased pressure, which probably increases the collisions between the molecules, and thus gives rise to a larger number

of phases of vibration. Thus, $H_2 + O$ fired in a closed space gives a continuous spectrum.

Fig. 206.
Geissler tube.

Hence arises the custom of examining the spectrum of a gas at much diminished pressure in a Geissler tube (Fig. 206). This consists of a tube very much constricted at the middle part of its length and having electrodes of aluminium sealed through the glass. The tube is first exhausted by the air-pump, and then a small quantity of the gas to be examined, sufficient to create a pressure of a few millimetres, is admitted. The electrodes are connected with the terminals of a powerful induction coil, and the spectroscope is directed to the constricted part of the tube for examination of the spectrum of the gas.

When the vapour whose spectrum is to be examined is heated by contact with a flame (as in the method for obtaining the spectra of metallic vapours described above), chemical reactions will frequently render the spectrum

Fig. 207.—Radiant matter bulb.

different from that observed by volatilising the substance and heating the vapour by electric sparks (*spark spectrum*). Thus, when cupric chloride is introduced into the Bunsen flame, the reducing action of

Fig. 208.—Air-pump.

the gases causes the spectrum to contain a blue line due to cuprous chloride, a green line due to cuprous oxide, and a red line due to copper, together with the other, fainter lines characteristic of these vapours.

A gas will absorb those wave lengths from the spectrum which it will itself emit when heated. Thus, if white light be passed through sodium vapour and then through a prism, black lines in the position of wave lengths 589.5 and 588.9 millionths of a millimetre will appear in the spectrum.

The black lines in the solar spectrum are presumed to be due to the light passing through gaseous elements surrounding the sun. Such *absorption spectra* are also exhibited by some solutions, such as solutions of didymium salts, of blood and of many dyes. Analytical use may be made of these for identifying the substance in solution.

Another method for obtaining a characteristic spectrum is to expose the substance in a vacuous glass bulb (Fig. 207) to a high pressure electrical discharge (from an induction coil) delivered from two platinum electrodes, attached to wires of the same metal sealed through the glass. Many substances phosphoresce under this treatment, and when the light thus emitted is viewed through a spectroscope it exhibits bright bands which serve to identify the substance. A pump capable of creating, in a very short time, a sufficiently high vacuum for the observation of such phosphorescence is shown in Fig. 208.

CHEMISTRY OF THE METALS.

178. The definition of a metal has already been given at p. 38, as *an element capable of forming a base by union with oxygen.* It will also be noticed that the metals are but little disposed to form combinations with hydrogen; but that they evince very powerful attraction for the chlorine group of elements, with which they form, as a rule, compounds soluble, without apparent decomposition, in water.

With a few exceptions the metals will be considered in the same order as they occur in the families of the periodic grouping of the elements, to the table of which the reader must refer for a true classification of the metals.

POTASSIUM.

K′ = 39.1 parts by weight.

179. Potassium is found in abundance, as potassium chloride and sulphate, in certain salt-mines (see below), and is contained in granite, of which it forms about 5 or 6 per cent. The indispensable alkali, *potash*, appears to have been originally derived from the granite rocks, where it exists, in combination with silica and alumina, in the well-known minerals *felspar* and *mica*. These rocks having, in course of time, disintegrated to form soils for the support of plants, the potash has been converted into a soluble state, and has passed into the plants as a necessary portion of their food.

In the plant, the potash is found to have entered into various forms of combination; thus, most plants contain sulphate and chloride of potassium; but the greater portion of the potassium exists in the form of salts of certain vegetable acids formed in the plant, and when the latter is burnt, these salts are decomposed by the heat, leaving the potassium in the form of carbonate.

Potassium carbonate, or *carbonate of potash*, K_2CO_3.—When the ashes of plants are treated with water, the salts of potassium are dissolved, those of calcium and magnesium being left. On separating the aqueous solution and evaporating it to a certain point, a great deal of the potassium sulphate, being much less soluble, is deposited, and the carbonate remains in the solution; this is evaporated to dryness, when the carbonate is left, mixed with much potassium chloride, and some sulphate; this mixture constitutes the substances imported from America and other countries where wood (containing about 0.5 per cent. of K_2O) is abundant, under the name of *potashes*, which are much in demand for the manufacture of soap and glass. When further purified,

these are sold under the name of *pearlash*, but this is still far from being pure potassium carbonate.

During the fermentation of the grape-juice, in the preparation of wine, a hard crystalline substance is deposited, which is known in commerce by the name of *argol*, or, when purified, as *cream of tartar*. The chemical name of this salt is bitartrate of potash or hydropotassium tartrate, for it is derived from potash and tartaric acid, a vegetable acid having the composition $H_2C_4H_4O_6$. When this salt ($KHC_4H_4O_6$) is heated, it leaves potassium carbonate mixed with carbon; but if the heat be continued, and free access of air permitted, the carbon will be entirely burnt away, and potassium carbonate will be left (*salt of tartar*).

The residue left after the sugar has been extracted from the sugar beet is worked up for the potassium carbonate it contains by first charring it, extracting it with water, and fractionally crystallising the solution obtained; the sulphate and chloride of potassium crystallise first, leaving the K_2CO_3 in the mother liquor.

The fleeces of sheep contain about 50 per cent. of fatty matter (*suint* or *yolk*), rich in potassium combined with an organic acid; when the fleece is washed with water, this salt is dissolved out, and on evaporating the liquid and burning the residue this is converted into potassium carbonate.

Potassium carbonate is also made from potassium sulphate by a process similar to that by which sodium sulphate is converted into carbonate (see *Alkali Manufacture*). Potassium chloride is converted into potassium carbonate by heating it under pressure with magnesium carbonate and CO_2, whereby the salt $KHMg(CO_3)_2.4H_2O$ is obtained; when this is heated with water at 120° C. it yields insoluble $MgCO_3$ and a solution of K_2CO_3 which is evaporated.

Potassium carbonate is deliquescent and soluble in its own weight of cold water, yielding a strongly alkaline solution. It may be crystallised in prisms of the formula $2K_2CO_3.3H_2O$, which become $K_2CO_3.H_2O$ at 100° C. It is insoluble in alcohol. It melts at 830° C.

Bicarbonate of potash, or *hydropotassium carbonate*, $KHCO_3$, often sold as the carbonate and used in medicine, is made by saturating moist K_2CO_3 with CO_2, or by passing CO_2 through a strong solution of K_2CO_3 (in three parts of water). It forms prismatic crystals which are much less alkaline and less soluble in water (30.4 per cent. at 15° C.) than is the normal carbonate, into which they are converted by heat; $2KHCO_3 = K_2CO_3 + H_2O + CO_2$. The aqueous solution of $KHCO_3$ gradually loses CO_2 when boiled.

Caustic potash, or potassium hydroxide, KOH.—Potassium carbonate was formerly called potash, and was supposed to be an elementary substance. It was known that its alkaline qualities were rendered far more powerful by treating it with lime, which caused it to be termed *mild* alkali, in order to distinguish it from the *caustic* alkali obtained by means of lime, and possessed of very powerful corrosive properties.

The caustic potash, so largely employed by the soap-maker, is obtained by adding slaked lime ($Ca(OH)_2$) to a boiling solution of the potassium carbonate, in not less than 12 parts of water, when calcium carbonate is deposited at the bottom of the vessel, whilst *potassium hydrate* remains in the clear solution; $K_2CO_3 + Ca(OH)_2 = CaCO_3 + 2KOH$.

If the solution be too strong, the lime will not decompose the carbonate, for the reaction is reversible (p. 309).

When the solution is evaporated, the potassium hydroxide remains as a clear oily liquid, which solidifies to a white mass as it cools, and forms the fused potash of commerce, which is often cast into cylindrical sticks for more convenient use.* Potassium hydroxide is vapourised at high

* These have sometimes a greenish colour, due to the presence of some potassium manganate.

temperatures without decomposition. It readily absorbs water and CO_2 from the air. Half its weight of water suffices to dissolve it, with great evolution of heat. A strong solution deposits crystals of KOH.2Aq. Alcohol dissolves it easily. The potassium hydroxide is the most powerful alkaline substance in ordinary use, and is much used by the chemist, generally in the state of solution, the strength of which is inferred from its specific gravity, which increases with the amount of potash contained in the solution.

Potassium.—Of the composition of potassium hydroxide nothing was known till the year 1807, when Davy succeeded in decomposing it by the galvanic battery; this experiment, which deserves particular notice as being the first of a series resulting in the discovery of so many important metals, was made in the following manner: A fragment of potassium hydroxide, which, in its dry state, does not conduct electricity, was allowed to become slightly moist by exposure to the air, and placed upon a plate of platinum attached to the copper end of a very powerful galvanic battery; when the wire connected with the zinc end was made to touch the surface of the hydrate, some small metallic globules resembling mercury made their appearance at the extremity of this (negative) wire, at which the hydrogen contained in the hydroxide was also eliminated, whilst bubbles of oxygen were separated on the surface of the platinum plate connected with the positive wire (see p. 324). By allowing the negative wire to dip into a little mercury contained in a cavity at the surface of the potash, a combination of potassium with mercury was obtained, and the mercury was afterwards separated by distillation. This process, however, furnished the metal in very small quantities, and, though it was obtained with greater facility a year or two afterwards by decomposing potassium hydroxide with white-hot iron, some years elapsed before any considerable quantity of potassium was prepared by the present method of distilling in an iron retort an intimate mixture of potassium carbonate and carbon, obtained by calcining cream of tartar; in this process the oxygen of the carbonate is removed by the carbon in the form of carbonic oxide ($K_2CO_3 + C_3 = K_2 + 3CO$).

The metal thus prepared requires re-distillation in order to decompose the explosive compound of potassium with carbon monoxide, $K_6(CO)_6$, which it always contains.

Some of the most striking properties of this metal have already been referred to (p. 16); its softness, causing it to be easily cut like wax, the rapidity with which its silvery surface tarnishes when exposed to the air, its great lightness (sp. gr. 0.865), causing it to float upon water, and its taking fire when in contact with that liquid, sufficiently distinguish it from other metals. It fuses at 62°.5 C. and boils at a low red heat (667° C.), yielding a green vapour; if air be present, it burns with a violet-coloured flame, the oxide K_2O_4 being the chief product. In *dry* air or oxygen the metal may be distilled unchanged.

The property of burning with this peculiar violet-coloured flame is characteristic of potassium, and allows it to be recognised in its compounds.

If a solution of potassium nitrate (saltpetre) in water be mixed with enough spirit of wine to allow of its being inflamed, the flame will have a peculiar lilac colour. This colour may also be developed by exposing a very minute particle of

saltpetre, taken on the end of a heated platinum wire, to the reducing (inner) blowpipe flame (Fig. 209), when the potassium, being reduced to the metallic state and passing into the oxidising (outer) flame in the state of vapour, imparts to that flame a lilac tinge.

The difficulty and expense attending the preparation of potassium have prevented its receiving any application except in purely chemical

Fig. 209.—Coloured flame test.

operations, where its attraction for oxygen, chlorine, and other electro-negative elements is often turned to account.

Potassium hydride, K_2H, is formed when potassium is heated in hydrogen to about 350° C. It forms a silvery brittle mass, which takes fire in air and is dissociated in a vacuum at 200° C.

Oxides of Potassium.—K_2O, is alleged to be formed when K is heated with KOH, H being expelled, but the evidence as to the existence of this oxide is very poor. *Potassium tetroxide*, K_2O_4, is the yellow powder obtained when the metal is heated in air or oxygen. It is decomposed by water yielding the *dioxide*, K_2O_2, and evolving O. By heating potassium in a limited supply of nitrous oxide, the *trioxide*, K_2O_3, is formed as a buff powder.

Potassium chloride (KCl) is an important natural source of this metal, occurring in combination with magnesium chloride as the mineral *carnallite* ($KCl.MgCl_2.6H_2O$), an immense saline deposit overlying the rock-salt in the salt-mines of Stassfurt, in Saxony. Carnallite resembles rock-salt in appearance, but is very deliquescent. It yields a magma of KCl crystals when treated with water; this is re-crystallised. Potassium chloride crystallises in anhydrous cubes; it is very soluble in water and insoluble in alcohol; it melts at 734° C. By melting KCl with potassium a blue *subchloride* K_2Cl is alleged to be obtained; it decomposes water evolving H.

Potassium chlorate, $KClO_3$, is prepared as described at page 185. It is also made by electrolysing a solution of KCl, but the methods are kept secret; the principle underlying them is noticed in the section on soda. It crystallises in four-sided tables, soluble in 16 parts of cold and 2 parts of boiling water. It fuses at 360° C., and is decomposed at 400°, when it gives off oxygen, and leaves, at first, a mixture of chloride and perchlorate, and lastly chloride only; $2KClO_3 = KClO_4 + KCl + O_2$. Its action on combustible bodies and consequent useful applications have been described at p. 186.

Potassium perchlorate, $KClO_4$, is remarkable for its sparing solubility, for it requires 70 parts of cold water to dissolve it. It is prepared by heating $KClO_3$ until 12 grams have evolved a litre of oxygen, as shown in the above equation; the mass is boiled with just enough water to dissolve it, and the solution, on cooling,

deposits crystals of $KClO_4$, leaving the KCl in solution. The perchlorate is decomposed above 400° C. into KCl and O_4.

Potassium bromide, KBr (m. p. 699° C.), forms cubical crystals very soluble in water.

Potassium iodide, KI, is prepared by adding iodine in small quantities to solution of potash till it is coloured slightly brown, when a mixture of potassium iodide and iodate is obtained; $6KOH + I_6 = KIO_3 + 5KI + 3H_2O$. The solution is evaporated to dryness, the residue mixed with one-tenth of its weight of powdered charcoal, thrown in small quantities into a red-hot iron crucible and fused; $KIO_3 + C_3 = KI + 3CO$. The fused mass is dissolved in hot water, filtered, evaporated till a film appears upon the surface, and set aside to crystallise. It is also made by digesting iron filings with iodine and water, and decomposing the solution of ferrous iodide, which is formed, with potassium carbonate.

Potassium iodide forms cubical crystals very soluble in water, but sparingly soluble in alcohol. It is of the greatest importance in medicine, in chemical analysis, and in photography. It melts at 634° C.

Potassium tri-iodide, KI_3, obtained by saturating potassium iodide with iodine and evaporating over sulphuric acid, forms dark brown needles with a metallic lustre, very deliquescent, and easily decomposed into KI and I_2.

Potassium iodate, KIO_3, is useful in testing for SO_2, and may be prepared for that purpose by mixing 50 grains of iodine with an equal weight of potassium chlorate in fine powder, adding, in a flask, about half a measured ounce of nitric acid, and digesting till the colour disappears. The liquid is then boiled for a minute, poured into a dish, evaporated to dryness, and moderately heated, when it leaves a mixture of potassium iodate and a little potassium chloride which may be dissolved in water. SO_2 at once liberates iodine from it, which gives a blue colour to starch.

Potassium fluoride, KF (m. p. 789° C.), is prepared by neutralising HF with K_2CO_3. Crystallised by slow evaporation of a cold solution, it gives $KF.2H_2O$, but above 35° C. it yields cubes of KF. It is deliquescent and easily soluble; the solution corrodes glass. It combines with HF, forming KF.FH, which is employed for the preparation of pure HF.

Potassium sulphide, K_2S, is obtained as a red crystalline mass by heating K_2SO_4 in hydrogen. Solution of K_2S is prepared by saturating solution of KOH with H_2S, and adding an equal quantity of KOH. From the solution, colourless crystals of $K_2S.5H_2O$ may be obtained; they deliquesce in air and are decomposed by the CO_2 therein with evolution of H_2S.

Potassium hydrogen sulphide, KSH, may be formed by saturating a strong solution of KOH with H_2S and evaporating *in vacuo*, when colourless deliquescent crystals, $2KSH.H_2O$, separate. On exposure to air the solution of KHS evolves H_2S owing to the action of CO_2; if the air be free from CO_2 the solution is oxidised to potassium thiosulphate, $K_2S_2O_3$.

Potassium sulphate, K_2SO_4, is found in certain salt-mines, in the mineral *kainit*, $K_2SO_4.MgSO_4.MgCl_2.6Aq$. This is decomposed by adding KCl, whereupon all the $MgSO_4$ becomes $MgCl_2$, and crystallising from water when the K_2SO_4 crystallises, on cooling, in rhombic prisms which are rather sparingly soluble in cold water (10 parts), but easily in boiling water (4 parts). It is also obtained as a by-product in some chemical manufactures, and is used in making alum. It melts at 1066° C. Kainit is largely used as an artificial manure.

Bisulphate of potash, or *hydrogen-potassium sulphate*, $KHSO_4$, is obtained as the residue in the preparation of nitric acid from saltpetre. It is more fusible and more soluble in water than the normal sulphate

is. Its solution is strongly acid. Much water decomposes it into sulphuric acid and K_2SO_4. When heated, it undergoes decomposition in two stages: (1) $2KHSO_4 = H_2O + K_2S_2O_7$ (*pyrosulphate* or *anhydrosulphate*); (2) $K_2S_2O_7 = K_2SO_4 + SO_3$. This evolution of SO_3 makes the bisulphate very useful in chemical operations for decomposing minerals at high temperatures.

Potassium nitrate (KNO_3), or *saltpetre*, is found in India, especially in Bengal and Oude, and other hot climates, where it sometimes appears in the dry season as a white incrustation on the surface of the soil, and is sometimes mixed with the soil to some depth. The nitre is extracted from the earth by treating it with water, and the solution is evaporated, at first by the heat of the sun, and afterwards by artificial heat, when the impure crystals are obtained, which are packed in bags and sent to this country as *grough* (or impure) saltpetre. It contains a quantity of extraneous matter varying from 1 to 10 per cent., and consisting of the chlorides of potassium and sodium, sulphates of potassium, sodium, and calcium, vegetable matter from the soil, sand, and moisture. The number representing the percentage of impurity present is usually termed the *refraction* of the nitre, in allusion to the old method of estimating it by casting the melted nitre into a cake and examining its fracture, the appearance of which varies according to the amount of foreign matter present.

Potassium nitrate is also made by decomposing sodium nitrate with potassium chloride.

In order to understand this decomposition, it is necessary to be acquainted with the solubility of these salts and of those produced by exchange of their elements.

100 parts of boiling water dissolve			100 parts of cold water dissolve		
180	parts of	sodium nitrate	80	parts of	sodium nitrate
57	,,	potassium chloride	28	,,	potassium chloride
240	,,	potassium nitrate	30	,,	potassium nitrate
37	,,	sodium chloride	36	,,	sodium chloride

It is a general rule that when two salts in solution are mixed, which are capable of forming, by exchange of their metals, a salt which is less soluble in the liquid, that salt will be produced and separated.

Thus, when sodium nitrate and potassium chloride are mixed, and the solution boiled down, sodium chloride is deposited, and potassium nitrate remains in the boiling liquid: $NaNO_3 + KCl = KNO_3 + NaCl$. When this is allowed to cool, the greater part of the potassium nitrate crystallises, leaving the remainder of the sodium chloride in solution.

The method usually adopted is to add the potassium chloride by degrees to the boiling solution of sodium nitrate, to remove the sodium chloride with a perforated ladle in proportion as it is deposited, and after allowing the liquid to rest for some time to deposit suspended impurities, to run it out into the crystallising pans.

Potassium nitrate was at one time prepared from the nitrates obtained in *nitre-heaps*, which consist of accumulations of vegetable and animal refuse, with limestone, old mortar, ashes, &c. These heaps are constructed upon an impermeable clay floor under a shed to protect them from rain. One side of the heap is usually vertical and exposed to the prevailing wind, the other side being cut into steps or terraces. They are occasionally moistened with stable drainings, which are allowed to run into grooves cut in the steps at the back of the heap. In such a mass, at an atmospheric temperature between 60° and 70° F., nitrates of the various metals present in the heap are slowly formed, and, being dissolved by the moisture, are left by it, as it evaporates on the vertical side, in the form of an efflorescence. When this has accumulated in sufficient quantity, it is scraped off, together with a few inches of the *nitrified* earth, and extracted with water, which dissolves the nitrates, whilst the undissolved earth is built up again on

the terraced back of the heap. After two or three years the heap is entirely broken up and reconstructed. The principal nitrates which are found dissolved in the water are those of potassium, calcium, magnesium and ammonium, the three last of which may be converted into potassium nitrate by decomposing them with potassium carbonate.

The formation of nitrates in these heaps is probably the result of chemical changes similar to those which occur in the soils in which nitre is naturally formed. the nitrates being produced by the oxidation, under the influence of the nitrifying organism (p. 88), of ammonia (page 88) evolved by the putrefaction of the nitrogenised matters which the heaps contain. The oxidation is much promoted by the presence of the strongly alkaline lime and of the porous materials capable of absorbing ammonia and presenting it under circumstances favourable to oxidation.

In *refining saltpetre* for the manufacture of gunpowder, the impure (*grough*) salt is dissolved in about an equal weight of boiling water in a copper boiler, the solution run through cloth filters to remove insoluble matter, and allowed to crystallise in a shallow wooden trough lined with copper, the bottom of which is formed of two inclined planes (Fig. 210). Whilst cooling, the solution is kept in continual agitation with wooden stirrers, in order that the saltpetre may be deposited in the minute crystals known as *saltpetre flour*, and not in the large prisms which are formed when the solution is allowed to crystallise tranquilly, and which contain within them cavities enclosing some of the impure liquor from which the saltpetre has been crystallised.

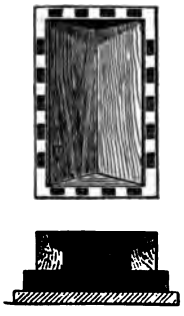


Fig. 210.

The saltpetre, being so much less soluble in cold than in hot water, is, in great part, deposited as the liquid cools, whilst the chlorides and other impurities, being present in small proportion, and not presenting the same disparity in their solubility at different temperatures, are retained in the liquid. The saltpetre flour is drained and washed with two or three successive small quantities of water; it is then allowed to drain thoroughly, and in that state, containing from 3 to 6 per cent. of water, according to the season, is ready to be transferred to the incorporating mill or to a hot-air oven, where it is dried if not required for immediate use.

The impurities most objectionable in saltpetre for gunpowder are KCl and NaCl, which absorb moisture from the air. Potassium perchlorate, $KClO_4$, is also liable to be present in the saltpetre, and is said to have led to spontaneous explosion of powder made with such saltpetre.

Potassium nitrate is usually distinguishable by the long striated or grooved six-sided prismatic form in which it crystallises (though it may also be obtained in rhombohedral crystals like those of sodium nitrate), and by the *deflagration* which it produces when thrown on red-hot coals. Its solubility in water has been given at p. 337. It is insoluble in alcohol. It fuses at 339° C. to a colourless liquid, which solidifies on cooling to a translucent brittle crystalline mass. The *sal prunelle* of the shops consists of nitre which has been fused and cast into balls. At a red heat it effervesces from the escape of bubbles of oxygen, and is converted into *potassium nitrite* (KNO_2), which is itself decomposed by a higher temperature, evolving nitrogen and oxygen, and leaving a mixture of potassium oxides. The fused salt attacks all oxidisable bodies and the potassium oxide attacks siliceous bodies, so that it is difficult to find a vessel capable of resisting it at a high temperature. Platinum gives way, but gold is less corroded. In contact with any

combustible body, it undergoes decomposition with great rapidity, five-sixths of its oxygen being available for the oxidation of the combustible substance, and the nitrogen being evolved in a free state; thus, in contact with carbon, the complete decomposition of the nitre may be represented by the equation $2KNO_3 + C_3 = K_2CO_3 + CO_2 + CO + N_2$. Since the combustion of a large quantity of material may be thus effected in a very small space and in a short time, the temperature produced is much higher than that obtained by burning the combustible in the ordinary way.

The specific gravity of saltpetre is 2.07, so that 1 c.c. weighs 2.07 grams. Since 202 grams (2 molecules) of nitre contain 80 grams (5 atoms) of oxygen available for the oxidation of combustible bodies, 2.07 grams (or 1 c.c. of nitre) would contain 0.8 gram (or 555 c.c.) of available oxygen, a volume which would be contained in about 2700 c.c. of air; hence, 1 volume of saltpetre represents, in its power of supporting combustion, 2700 volumes of atmospheric air. It also enables some combustible substances to burn without actual flame, as is exemplified by its use in *touchpaper* or *slow portfire*, which consists of paper soaked in a weak solution of saltpetre and dried, the combustion taking place between the *solid* combustible and the *solid* oxygen in the nitre instead of between gases as in the case of flame.

If a continuous design be traced on foolscap paper with a brush dipped in a solution of 30 grams of saltpetre in 100 grams of water, and allowed to dry, it will be found that when one part of the pattern is touched with a red-hot iron it will gradually burn its way out, the other portion of the paper remaining unaffected. A mixture of 6 grams of KNO_3, 2 of sulphur, and 2 of moderately fine dried sawdust (*Baumé's flux*) will deflagrate with sufficient intensity to fuse a small silver coin into a globule; the mixture may be pressed down in a walnut-shell or a small porcelain crucible, and the coin buried in it, the flame of a lamp being applied outside until deflagration commences.

Pulvis fulminans (*white gunpowder*) is a mixture of 3 parts of KNO_3, 1 part of sulphur, and 2 of K_2CO_3, all carefully dried; when it is heated on an iron plate no action occurs till it melts, when it explodes very violently.*

Gunpowder is a very intimate mixture of saltpetre, sulphur, and charcoal, which do not act upon each other at the ordinary temperature, but, when heated together, arrange themselves into new forms, evolving a very large amount of gas.

The great attention that has been paid to the manufacture of gunpowder is due to the fact that until recently it was the sole explosive available for warfare. Now, however, it may be said to be displaced by the various forms of "smokeless powders" which are all products of nitration (p. 94) of organic substances. Gunpowder is now made almost solely for use as a blasting explosive for mining.

The proportions of the ingredients of gunpowder have been varied somewhat in different countries, the saltpetre ranging from 74 to 77 per cent., the charcoal from 12 to 16 per cent., and the sulphur from 9 to 12.5 per cent. English military powder contains 75 per cent. of nitre, 15 per cent. of charcoal, and 10 per cent. of sulphur. Mining powder contains about 67 per cent. of nitre, 19 per cent. of charcoal, and 14 per cent. of sulphur.

The powdered ingredients† are first roughly mixed in a revolving gun-metal drum, with mixing arms turning in an opposite direction, and the mixture is subjected, in quantities of about 50 lbs at a time, to the action of the *incorporating mill*

* Probably $2KNO_3 + K_2CO_3 + S_2 = K_2SO_4 + K_2S + CO_2 + NO + NO_2$. The NO and NO_2 would probably be decomposed into their elements by the high temperature attained.

† The amount of water in the moist saltpetre (p. 338) is ascertained by drying and melting a weighed sample before the proportions are weighed out.

(Fig. 211), where it is sprinkled with water, poured through the funnel (*F*), or from a can with a fine rose, and exposed to trituration and pressure under two cast-iron edge-runners (B), rolling in different circular paths upon a cast-iron bed, a very intimate mixture being thus effected by the same kind of movement as in a common pestle and mortar, the distribution of the nitre through the mass being also assisted by its solubility in water. A wooden scraper (C) tipped with copper prevents the roller from getting clogged, and a *plough* (D) keeps the mixture in the path. Of course, the water employed to moisten the powder must be as free from deliquescent salts (especially chlorides, see page 338) as possible; at Waltham, condensed steam is employed: the quantity required varies with the state of the atmosphere. The duration of the incorporating process is varied according to the kind of powder required, the slow-burning powder employed for cannon being sufficiently incorporated in about three hours, whilst rifle-powder requires five hours.

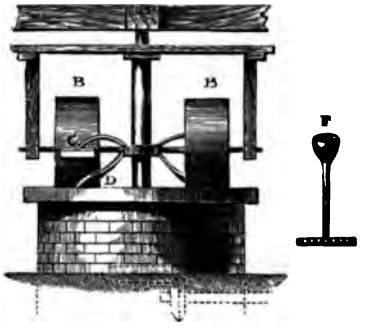


Fig. 211.—Incorporating mill.

The dark grey mass of *mill-cake* which is thus produced contains 2 or 3 per cent. of water. It is broken up by passing between grooved rollers of gun-metal, and is then placed, in layers of about half an inch thick, between copper plates packed in a stout gun-metal box lined inside and outside with wood, in which it is subjected for a quarter of an hour to a pressure of about 70 tons on the square foot, in a hydraulic press, which has the effect of condensing a larger quantity of explosive material into a given volume, and of diminishing the tendency of the powder to absorb moisture from the air, and to disintegrate or *dust* after granulation. The *press-cake* thus obtained is very hard and compact, resembling slate in appearance. As far as its chemical nature is concerned it is finished gunpowder, but if it be reduced to powder and a gun loaded with it, the combustion of the charge is found to occur too slowly to produce its full effect, since the pulverulent form offers so great an obstacle to the passage of the flame by which the combustion is communicated from one end of the charge to the other. The press-cake must, therefore, be *granulated* (*corned*) or broken up into grains of sufficient size to allow the rapid passage of the flame between them, and the consequent rapid firing of the whole charge. The granulation is effected by crushing the press-cake between successive pairs of toothed gun-metal rollers, from which it falls on to sieves, which separate it into grains of different sizes, the dust, or *meal powder*, passing through the last sieve. The granulated powders are freed from dust by passing them through revolving cylinders of wooden framework covered with canvas or wire cloth, and the fine-grain powder is glazed by the friction of its own grains against each other in revolving barrels. The large-grain powders are sometimes glazed or *faced* with graphite, by introducing a little of that substance into the glazing-barrels with the powder. The powder is dried in a chamber heated by steam, very gradually, so as not to injure the grain, and is once more dusted in canvas cylinders before being packed.

When it is required that the powder shall burn rapidly the grains are made small, but where a slower combustion is required, as was the case with heavy ordnance which were too much strained by the rapid combustion of fine grain powder, the size of grain is much increased, being from ⅛ to 1½ inch or more in diameter. To the same end the percentage of sulphur, on which the inflammability of the powder depends, is reduced, and a charcoal carbonised at a low temperature, and therefore comparatively inflammable, is used. Thus *cocoa-powder*, or *brown-powder*, is made with 79 per cent. nitre, 2 per cent. sulphur, and 18 per cent. of lightly burnt charcoal. In mining powders, rapidity of combustion is desirable, so that the proportion of sulphur and charcoal is increased, as shown in the composition given above.

180. Good gunpowder is composed of hard angular grains, which do not soil the fingers, and have a perfectly uniform dark grey colour.

Its specific gravity (*absolute density*), as determined by the *densimeter*,* varies between 1.67 and 1.84, and its *apparent density* (obtained by weighing a given measure of the grain against an equal measure of water) varies from 0.89 to 0.94, so that a cubic foot will weigh from 55 to 58 lbs. When exposed to air of average dryness, gunpowder absorbs from 0.5 to 1 per cent. of water. In damp air it absorbs a much larger proportion, and becomes deteriorated in consequence of the saltpetre being dissolved, and crystallising upon the surface of the grains. Actual contact with water dissolves the saltpetre and disintegrates the grains. When very gradually heated in air, gunpowder begins to lose sulphur, even at 100° C., this ingredient passing off rapidly as the temperature rises, so that the greater part of it may be expelled without inflaming the powder, especially if the powder be heated in carbonic acid gas or hydrogen, to prevent contact with air. If gunpowder be suddenly heated to 600° F. (315° C.) in air, it explodes, the sulphur probably inflaming first; but out of contact with air a higher temperature is required to inflame it. The ignition of gunpowder by flame is not ensured unless the flame be flashed among the grains of powder; it often takes some time to ignite powder with the flame of a piece of burning paper or stick, but contact with a red-hot solid body inflames it at once. A heap of good powder, when fired on a sheet of white paper, burns without sparks and without scorching or kindling the paper, which should exhibit only scanty black marks of charcoal after the explosion. If the powder has not been thoroughly incorporated, it will leave minute globules of fused nitre upon the paper. Two ounces of the powder should be capable of throwing a 68-lb. shot to a distance of 260 to 300 feet from an 80-inch mortar at 45° elevation.

Very fortunately, it is difficult to explode gunpowder by concussion, though it has been found possible to do so, especially on iron, and accidents appear to have been caused in this way by the iron edge-runners in the incorporating mill, when the workmen have neglected the special precautions which are laid down for them. The use of stone upon iron in the incorporation is avoided, because of the great risk of producing sparks, and copper is employed in the various fittings of a powder-mill wherever it is possible.

The electric spark is, of course, capable of firing gunpowder, though it is not easy to ensure the inflammation of a charge by a spark unless its conducting power is slightly improved by mixing it with a little graphite, or by keeping it a little moist, which may be effected by introducing a minute quantity of calcium chloride.

181. PRODUCTS OF EXPLOSION OF GUNPOWDER.—In the explosion of gunpowder, the oxygen of the nitre converts the carbon of the charcoal chiefly into carbon dioxide (CO_2), part of which assumes the gaseous state, whilst the remainder is converted into potassium carbonate (K_2CO_3). The greater part of the sulphur is converted into potassium sulphate (K_2SO_4). The chief part of the nitrogen contained in the nitre is evolved in the uncombined state. The rough chemical account of the explosion of gunpowder, therefore, is that the mixture of nitre, sulphur, and charcoal is resolved into a mixture of potassium carbonate, potassium sulphate, carbon dioxide, and nitrogen, the two last being gases, the elastic force of which, when expanded by the heat of the combustion, accounts for the mechanical effect of the explosion.

But in addition to these, several other substances are found among the products of the explosion. Thus, the presence of potassium sulphide (K_2S) may be recognised by the smell of hydrogen sulphide produced on moistening the solid residue in the barrel of a gun, and hydrogen sulphide (H_2S) itself may often be perceived in the gases produced by the explosion, the hydrogen being derived from the charcoal. A little marsh gas (CH_4) is also found among the gases, being produced

* This is a simple apparatus for determining the weight of mercury displaced by a given weight of gunpowder, from which all the air has been exhausted.

by the decomposition of the charcoal, a portion of the hydrogen of which is also disengaged in the free state. Carbonic oxide (CO) is always detected among the products. It is evident that the collection for analysis of the products of explosion must be attended with some trouble, and that considerable differences are to be expected between the results obtained by different operators, from the variation of the circumstances under which the powder is fired and the products collected. When the powder is slowly fired, a considerable proportion of the nitrogen in the saltpetre is evolved in the form of nitric oxide gas (NO), which is not found among the products of the rapid explosion of powder.

The period over which the combustion of a given weight of powder extends will, of course, depend upon the area of surface over which it can be kindled; thus a single fragment of powder weighing 10 grains, even if it were instantaneously kindled over its entire surface, could not evolve so much gas in a given time as if it had been broken into 10 separate grains, each of which was kindled at the same instant, since the inside of the large fragment can only be kindled from the outside. Upon this principle a given weight of powder in large grains will occupy a longer period in its explosion than the same weight in small grains, so that the large grain powder is best fitted for ordnance, where the ball is very heavy, and the time occupied in moving it will permit the whole of the charge to be fired before the ball has left the muzzle, whilst in small arms with light projectiles, a finer-grained and more quickly burning charge is required. If the fine-grain powder were used in cannon, the whole of the gas might be evolved before the containing space had been sensibly enlarged by the movement of the heavy projectile, and the gun would be subjected to an unnecessary strain; on the other hand, a large grain powder in a musket would evolve its gas so slowly that the ball might be expelled with little velocity by the first half of it, and the remainder would be wasted. There is good reason to believe that even under the most favourable circumstances a large proportion of every charge of powder is discharged unexploded from the muzzle of the gun and is therefore wasted. In blasting rocks and other mining operations, the space within which the powder is confined is absolutely incapable of enlargement until the gas evolved by the combustion has attained sufficient pressure to do the whole work, that is, to rend the rock, for example, asunder. Accordingly, a slowly burning charge will produce the effect, since the rock must give way when the gas attains a certain pressure, whether that happen in one second or in ten. Indeed, a slowly burning charge is advantageous, as being less liable to shatter the rock or coal, and bringing it away in larger masses with less danger. Barium nitrate and sodium nitrate are sometimes substituted for a part of the potassium nitrate in mining powder, its combustion being thus retarded.

The same charge of the same powder produces very different results when heated in different ways. If 5 grains of gunpowder be placed in a wide test-tube and fired by passing a heated wire into the tube, a slight puff only is perceived; but if the same amount of powder be heated in the tube by a spirit lamp, it will explode with a loud report, and perhaps shatter the tube (a copper or brass tube is safer). In the first place, the combustion is propagated slowly from the particle first touched by the wire; in the second, all the particles are raised at once to pretty nearly the same temperature, and as soon as one explodes, all the rest follow instantaneously.

When gunpowder is slowly fired, the products of its decomposition are different from those mentioned above; thus, nitric oxide (NO), arising from incomplete decomposition of the nitre, is perceived in considerable quantity, and may be recognised by the red colour produced when it is brought in contact with air.

The white smoke arising from the explosion of gunpowder consists chiefly of the sulphate and carbonate of potassium in a very finely divided state: it seems probable that at the instant of explosion they are converted into vapour, and are afterwards deposited in a state of minute division as the temperatute falls. From this it will be obvious that a powder that is required to be *smokeless* must be free from such saline products of explosion (see *Nitro-glycerine*). The *fouling* or actual solid residue in the gun is very trifling when the powder is dry and has been well incorporated: a damp or slowly burning powder leaves, as might be expected, a large residue. The residue always becomes wet on exposure to air, from the great attraction for moisture possessed by the carbonate and sulphide of potassium.

From the circumstance that the combustion of gunpowder is independent of any supply of oxygen from the air, it might be supposed that it would be as easily

inflamed *in vacuo* as under ordinary atmospheric pressure. This is not found to be the case, however, for a mechanical reason, viz., that the flame from the particles which are first ignited escapes so rapidly into the vacuous space that it does not inflame the more remote particles. For a similar reason, charges of powder in fuses are found to burn more slowly under diminished atmospheric pressure, the flame (or heating gas) escaping more rapidly and igniting less of the remaining charge in a given time. It has been determined that if a fuse be charged so as to burn for thirty seconds under ordinary atmospheric pressure (30 inches barometer), each diminution of 1 inch in barometric pressure will cause a delay of 1 second in the combustion of the charge, so that the fuze will burn for thirty-one seconds when the barometer stands at 29 inches.

SODIUM.

Na′ = 23 parts by weight.

182. Sodium is often found, in place of potassium, in the felspars and other minerals, but we are far more abundantly supplied with it in the form of *common salt* (sodium chloride, NaCl), occurring not only in the solid state, but dissolved in sea water, and in smaller quantity in the waters derived from most lakes, rivers, and springs.

Rock-salt forms very considerable deposits in many regions; in this country the most important is situated at Northwich, in Cheshire, where very large quantities are extracted by mining. Wielitzka, in Poland, is celebrated for an extensive salt-mine, in which there are a chapel and dwelling-rooms, with furniture made of this rock. Extensive beds of rock-salt also occur in France, Germany, Hungary, Spain, Abyssinia, and Mexico. Perfectly pure specimens form beautiful colourless cubes, and are styled *sal gemme;* but ordinary rock-salt is only partially transparent, and exhibits a rusty colour, due to the presence of iron. In some places the salt is extracted by boring a hole into the rock and filling it with water, which is pumped up when saturated with salt, and evaporated in boilers, the minute crystals of salt being removed as they are deposited.

At Droitwich, in Worcestershire, the salt is obtained by evaporation from the waters of certain salt springs. In some parts of France and Germany the water from the salt springs contains so little salt that it would not pay for the fuel necessary to evaporate the water, and a very ingenious plan is adopted by which the proportion of water is greatly reduced without the application of artificial heat. For this purpose a lofty scaffolding is erected and filled with bundles of brushwood, over which the salt water is allowed to flow, having been raised to the top of the scaffolding by pumps. In trickling over the brushwood this water exposes a large surface to the action of the wind, and a considerable evaporation occurs, so that a much stronger brine is collected in the reservoir beneath the scaffolding; by several repetitions of the operation, the proportion of water is so far diminished that the rest may be economically evaporated by artificial heat. In England the brine (containing about 22 per cent. of salt) is run into large pans and rapidly boiled for about thirty hours, fresh brine being allowed to flow in continually, so as to maintain the liquid at the same level in the boiler. During this ebullition a considerable deposit, composed of the sulphates of calcium and sodium, is formed, and raked out by the workmen. When a film of crystals of salt begins to form upon the surface the fire is lowered, and the temperature of the brine allowed to fall to

about 82° C., at which temperature it is maintained for several days whilst the salt is crystallising. The crystals are afterwards drained, and dried by exposure to air. The grain of the salt is regulated by the temperature at which it crystallises, the size of the crystals increasing as the temperature falls. The coarsest crystals thus obtained are known in commerce as *bay-salt*. It is not possible to extract the whole of the salt in this way, since the last portions which crystallise will always be contaminated with other salts present in the brine; but the *mother-liquor* is not wasted, for after as much salt as possible has been obtained, it is made to yield sodium sulphate (Glauber's salt), magnesium sulphate (Epsom salts), bromine, and iodine.

The process adopted for extracting the salt from sea water depends upon the climate. In Russia, shallow pits are dug upon the shore, in which the sea water is allowed to freeze, when a great portion of the water separates in the form of pure ice, leaving a solution of salt sufficiently strong to pay for evaporation.

Where the climate is sufficiently warm, the sea water is allowed to run very slowly through a series of shallow pits upon the shore, where it becomes concentrated by spontaneous evaporation, and is afterwards allowed to remain for some time in reservoirs in which the salt is deposited. Before being sent into the market, it is allowed to drain for a long time, in a sheltered situation, when the magnesium chloride with which it is contaminated deliquesces in the moisture of the air and drains away. The *bittern*, or liquor remaining after the salt has been extracted, is employed to furnish magnesia and bromine.

1000 parts of sea water contain about 29 parts of NaCl, 0.5 of KCl, 2 of $MgCl_2$, 2.5 of $MgSO_4$, 1.5 of $CaSO_4$, &c.

In a warm climate, that of Marseilles, for example, the water is allowed to evaporate spontaneously until it has a specific gravity of 1.24. During this operation it deposits about four-fifths of its sodium chloride. It is then mixed with one-tenth of its volume of water, and artificially cooled to 0° F. (see p. 82), when it deposits a quantity of sodium sulphate, resulting from the decomposition of part of the remaining sodium chloride by the magnesium sulphate. The mother-liquor is evaporated till its specific gravity is 1.33, a fresh quantity of sodium chloride being deposited during the evaporation. When the liquid cools, it deposits a double salt composed of chlorides of potassium and magnesium, from which the latter chloride may be extracted by washing with a very little water, leaving the potassium chloride fit for the market.

This process is instructive as illustrating the influence exerted upon the nature of the salts which will be deposited from a solution by the temperature to which this is exposed, the general rule being that that salt separates which is least soluble in the liquid at the particular temperature.

The great tendency observed in ordinary table salt to become damp when exposed to the air is due chiefly to the presence of small quantities of chlorides of magnesium and calcium, for pure sodium chloride has a very much smaller disposition to attract atmospheric moisture, although it is very easily dissolved by water, $2\frac{3}{4}$ parts being able to dissolve 1 part (by weight) of salt. The saturated solution boils at 107.5° C.

In the history of the useful applications of common salt is to be found one of the best illustrations of the influence of chemical research upon the development of the resources of a country, and a capital example of a manufacturing process not based, as such processes usually are, upon mere experience, independent of any knowledge of chemical principles, but upon a direct and intentional application of these to the attainment of a particular object.

Until the last quarter of the eighteenth century, the uses of common salt were limited to culinary and agricultural purposes, and to the glazing of the coarser kinds of earthenware, whilst a substance far more useful in the arts, *carbonate of soda*, was imported chiefly from Spain

under the name of *barilla*, which was the ash obtained by burning a marine plant known as the *salsola soda*. But this ash only contained about one-fourth of its weight of carbonate of soda, so that this latter substance was thus imported at a great expense, and the manufactures of soap and glass, to which it is indispensable, were proportionately fettered.

During the wars of the French Revolution the price of barilla had risen so considerably that it was deemed advisable by Napoleon to offer a premium for the discovery of a process by which the carbonate of soda could be manufactured at home, and to this circumstance we are indebted for the discovery, by Leblanc, of the process, which is only now being superseded, for the manufacture of carbonate of soda from common salt, a discovery which placed this substance at once among the most important raw materials with which a country could be furnished.

183. *Manufacture of sodium carbonate from common salt by the Leblanc process.*—This process consists in heating salt with sulphuric acid,

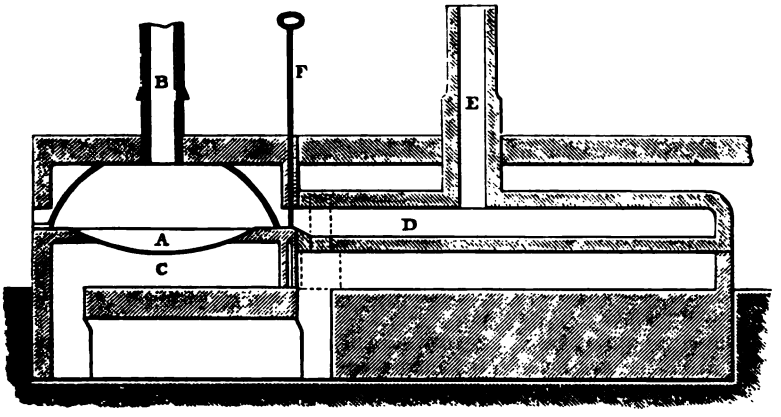


Fig. 212.—Furnace for converting common salt into sulphate of soda.

whereby sodium sulphate and hydrogen chloride are produced (see p. 177). The sodium sulphate, technically called *salt cake*, is then mixed with small coal and limestone, and again heated in order to convert it into sodium carbonate, a change which may be represented by the two equations:

$$\underset{\text{Sodium sulphate.}}{(1)\ Na_2SO_4} + C_2 = \underset{\text{Sodium sulphide.}}{Na_2S} + 2CO_2$$

$$(2)\ Na_2S + CaCO_3 = Na_2CO_3 + \underset{\text{Calcium sulphide.}}{CaS}$$

The resulting mixture of sodium carbonate and calcium sulphide, technically called *black ash*—being black from the presence of coal—is leached with water to dissolve the sodium carbonate and leave the calcium sulphide (*tank-waste*).* The liquor is evaporated to crystallise the sodium carbonate (*soda crystals*).

In the first part of the process (*salt cake process*) the salt is introduced into the iron pan, A, of a *salt cake furnace* (Fig. 212), where it is mixed with an equal weight of H_2SO_4 (sp. gr. 1.72) and heated by the fire in the grate, C. Much HCl is expelled and escapes through the flue B, whence it passes to the bottom of a brick tower

* The CaS in the waste is insoluble because combined with lime.

packed with coke down which water is trickled; the water absorbs the HCl from the gases as they ascend the tower, forming the muriatic acid of commerce (p. 178). The door F is then raised, and the partly decomposed salt raked from the pan into the brick *roaster* D: this is virtually a muffle heated by the flames from a furnace, which circulate in the flues surrounding it. The conversion of the salt into sodium sulphate is here completed, the remaining HCl escaping through the flue E to condensing towers similar to that described above.

In the second part of the process the mixture of ground salt cake (10 parts), limestone (10 parts), and small coal (4–6 parts) is heated in a *black ash furnace*, which is essentially a reverberatory furnace, such as is shown in Fig. 109.

When the black ash is treated with water, the sodium carbonate is dissolved, leaving the calcium sulphide,* and by evaporating the solution, and calcining the residue, ordinary *soda ash* is obtained.† But this is by no means pure sodium carbonate, for it contains, in addition to a considerable quantity of common salt and sodium sulphate, a certain amount of caustic soda, formed by the action of lime (formed from the heating of the excess of limestone used) upon the carbonate. In order to purify it, the crude soda ash is mixed with small coal or sawdust and again heated, when the carbonic acid gas formed from the carbonaceous matter converts the caustic soda into carbonate, and on dissolving the mass in water and evaporating the solution, it deposits oblique rhombic prisms of common washing soda, having the composition $Na_2CO_3.10Aq$ (*soda crystals*).

Hargreave's process dispenses with the use of sulphuric acid, and converts the sodium chloride into sulphate by the action of sulphurous acid gas (obtained by burning pyrites), steam, and air, at a dull red heat; $2NaCl + H_2O + SO_2 + O = Na_2SO_4 + 2HCl$. The hydrochloric acid is absorbed by water, as usual, and the sodium sulphate converted into carbonate as described above.

A little reflection will show the important influence which this process has exerted upon the progress of the useful arts in this country. The three raw materials, salt, coal, and limestone, we possess in abundance. The sulphuric acid, when the process was first introduced, bore a high price, but the resulting demand for this acid gave rise to so many improvements in its manufacture that its price has been very greatly diminished—a circumstance which has of course produced a most beneficial effect upon all branches of manufacture in which the acid is employed.

The large quantity of hydrochloric acid obtained as a secondary product has been employed for the preparation of bleaching-powder, and the important arts of bleaching and calico-printing have thence received a considerable impulse. These arts have also derived a more direct benefit from the increased supply of sodium carbonate, which is so largely used for cleansing all kinds of textile fabrics. The manufactures of soap and glass, which probably create the greatest demand for sodium carbonate, have been increased and improved beyond all precedent by the production of this salt from native sources.

Ammonia-soda process, or *Solvay's process*.—This process for converting NaCl into Na_2CO_3, which has almost completely superseded the Leblanc process, depends upon the reaction between sodium chloride, carbon dioxide, ammonia and water, $NaCl + NH_3 + CO_2 + H_2O = NaHCO_3 + NH_4Cl$. A solution of salt is saturated, first with ammonia and then with carbon dioxide, whereupon sodium hydrogen carbonate is precipitated. This is collected and calcined in order to convert it into *soda ash*; $2NaHCO_3 = Na_2CO_3 + H_2O + CO_2$. The solution containing NH_4Cl is heated with lime to recover the ammonia—

$$2NH_4Cl + CaO = 2NH_3 + H_2O + CaCl_2.$$

* The CaS in the waste is insoluble because combined with lime.

† Before evaporation, air is generally blown through the liquor to oxidise the sodium sulphide which may remain unaltered (see p. 348, *Sodium hydroxide*).

The brine pumped from the wells contains magnesium salts and other salts ; lime is added to remove these, and the excess of lime is precipitated by ammonium carbonate. The liquor is then saturated with salt by addition of pure salt, and with NH_3 by passing in this gas from the ammonia stills ; it is then made to flow down a vertical iron cylinder containing perforated shelves and kept cool by water. CO_2 is pumped up this cylinder and meets the descending liquor, from which $NaHCO_3$ is deposited and collected on the shelves, whence it falls as a sludge to the bottom of the cylinder. The liquor from which the $NaHCO_3$ has separated is run into the ammonia stills where it is heated with lime in order to recover the NH_3. The CO_2 used in the process is derived partly from the limekilns in which the lime for the ammonia stills is burnt, and partly from the calcining of the $NaHCO_3$ to get Na_2CO_3.

Recovery of waste in alkali manufacture.—It is obvious that it should be the object of every chemical manufacturer to utilise his raw materials in such a manner that none of the elements in them shall ultimately remain in an unmarketable form. A little reflection will show that in an ideal process for making alkali, the only component of the raw materials which should be finally rejected is the atmospheric nitrogen. In practice, however, there has been, until lately, a large source of waste in both the above processes. It will have been seen that in the Leblanc process the whole of the sulphur of the H_2SO_4 which is used makes its appearance as CaS in the tank waste; whilst in the ammonia-soda process all the chlorine in the salt makes its appearance as $CaCl_2$ in the ammonia-still liquor. The tank waste and still liquor were originally rejected, so that whilst the ammonia-soda process had the advantage over the Leblanc process that it did not pay for sulphur which was finally wasted, it had the accompanying disadvantage that it did not recover the chlorine of the salt, which is a source of profit to the Leblanc process. Whilst, therefore, CaS is the *alkali waste* of the older process, $CaCl_2$ is that of the newer process, although since the sulphur is now recovered from the CaS, and the Cl from the still liquor,* this term has become a misnomer. It must be added that much of the soda in black ash being in the form of caustic soda (see above), this product is more easily made by the Leblanc process than by the ammonia-soda process ; so that in many cases the Leblanc makers have ceased to produce sodium carbonate, and are now manufacturers of caustic alkali, bleaching-powder, and pure sulphur. The manufacture of chlorine and bleach have been sketched on pp. 170 and 183, and the recovery of manganese from the chlorine-still liquor on p. 170.

Recovery of sulphur from tank waste.—This is now effected by *Chance's process*, which depends upon the fact that when carbon dioxide (lime-kiln gases) is passed into alkali waste (CaS), made into a cream with water, H_2S is evolved and $CaCO_3$ remains; $CaS + H_2O + CO_2 = CaCO_3 + H_2S$.† The sulphuretted hydrogen is mixed with a carefully regulated supply of air and passed through a kiln (*Claus kiln*) containing some porous material, when the hydrogen alone is burnt, the sulphur being subsequently deposited in condensing-chambers; $H_2S + O = H_2O + S$. The $CaCO_3$ from this process is used again in making black ash.

Recovery of chlorine from ammonia-still liquor.—When lime is used in the ammonia stills calcium chloride remains in the liquor; it is difficult to recover chlorine from this compound. If magnesia be

* Exact information as to the recovery of chlorine is not divulged by the ammonia-soda makers, but it is believed to have been successfully effected.

† An elaborate, systematically worked plant is essential in order that the evolved gas may be as rich as possible in H_2S.

substituted for lime, magnesium chloride is left ($2NH_4Cl + MgO = 2NH_3 + H_2O + MgCl_2$), from which chlorine may be recovered by the *Weldon-Pechiney process*. This consists in mixing MgO with the concentrated $MgCl_2$ solution, whereby magnesium oxychloride ($5MgO.4MgCl_2$) is produced. This can be dried without losing HCl, which is not possible with $MgCl_2$ itself; and when the dried mass is heated in air at 1000° C., it gives up its chlorine in exchange for oxygen. The MgO thus left is used again.

Mond seeks to prepare the $MgCl_2$ in a nearly anhydrous state by volatilising the NH_4Cl and passing the vapour over heated MgO, whereby NH_3, H_2O, and $MgCl_2$ are produced; the first is used in the ammonia-soda plant, whilst the $MgCl_2$ may be heated in air to yield MgO and Cl, as described above. The NH_4Cl is obtained in crystals by cooling the mother-liquor from the towers in which the $NaHCO_3$ is precipitated (see above).

Sodium carbonate, *washing soda*, $Na_2CO_3.10Aq$.—The crystals of sodium carbonate are easily distinguished by their property of efflorescing in dry air (p. 52), and by their alkaline taste, which is much milder than that of potassium carbonate, this being, moreover, a deliquescent salt. The crystals are very soluble in water, requiring only 2 parts of cold, and less than their own weight of boiling water; the solution is strongly alkaline to test-papers. The crystals fuse at 50° C., evolve steam, and deposit a granular powder of the composition $Na_2CO_3.Aq$ (*crystal carbonate*). At a higher temperature it becomes Na_2CO_3, and fuses at 850° C. If a solution of sodium carbonate be crystallised between 30° and 50° C., the crystals are $Na_2CO_3.7Aq$. The mineral *natron* found at the soda lakes of Egypt is $Na_2CO_3.10Aq$. The chief impurities in soda crystals are NaCl and Na_2SO_4; soda ash may contain in addition NaOH and Na_2S.

Bicarbonate of soda, or *hydrogen sodium carbonate*, $NaHCO_3$, is the substance commonly used in medicine as carbonate of soda. It is prepared either by saturating the crystallised carbonate with CO_2, or by passing CO_2 through a strong solution of common salt mixed with ammonia (see p. 346).* It forms small prismatic crystals much less easily dissolved by water (8.85 per cent. at 15° C.) than the carbonate. The solution is much less alkaline. When the solution is heated it evolves CO_2, and crystals of the *sesquicarbonate* $Na_2CO_3.NaHCO_3.2Aq$, may be obtained from it. A similar salt is the mineral *Trona*. It has been seen that, when strongly heated, $2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O$.

Potassium sodium carbonate, $KNaCO_3.6Aq$, may be crystallised from a mixture of solutions of the carbonates.

Soda lye, employed in the manufacture of hard soap, is a solution of **sodium hydroxide** (NaOH), obtained by decomposing the carbonate with calcium hydroxide (slaked lime); $Na_2CO_3 + Ca(OH)_2 = 2NaOH + CaCO_3$. The solid NaOH of commerce, *caustic soda*, is prepared in the Leblanc alkali process; the solution obtained by treating the black ash with water is *causticised* with lime, as represented in the above equation, and concentrated by evaporation until it solidifies on cooling, at which stage it is poured out into iron moulds. In properties it closely

* A saturated solution of NaCl mixed with one-third of its volume of NH_3 (sp. gr. 0.88) and saturated with CO_2 gives a copious precipitate of $NaHCO_3$.

resembles KOH; its common impurities are carbonate, chloride, sulphate, and nitrite of sodium, sometimes accompanied by zinc oxide.

In practice, the *tank liquor* (from the black ash) is purified from sulphides before it is causticised, partly by blowing air through it which oxidises the sulphides, and partly by addition of zinc oxide which precipitates the sulphur as zinc sulphide. The removal of the other salts (sulphate and chloride) occurs when the caustic liquor is concentrated, for they then crystallise and may be fished out; the last traces of sulphide are oxidised by the addition of a little $NaNO_3$ to the melted NaOH before it is cast.

Electrolytic production of alkali and chlorine.—Since these main products of the alkali industry contain much more chemical energy than that of the salt from which they are derived, it is obvious that they can only be obtained by transferring the chemical energy of other substances, or by transforming some other kind of energy into chemical energy. In the foregoing processes both these methods of procuring the necessary energy are applied. There is an increasing tendency, however, to apply electrical energy directly to the salt and thus to convert it into the chemical energy of alkali and chlorine. There are certain conveniences in converting heat energy first into electrical energy, by means of a steam-engine and dynamo, and then applying this electrical energy directly instead of the heat energy. But the use of electrical energy has most to recommend it in places where dynamos can be driven by the energy of running water.

Two methods of using the electrical energy present themselves: (1) The current may be passed through fused salt, in which case the sodium chloride will be electrolysed with separation of the sodium at the cathode and chlorine at the anode. Since the heat of formation of salt is Na,Cl = 97,700 (p. 306), the electrical energy supplied must be the equivalent of this heat energy. (2) The current may be used to electrolyse a solution of salt, in which case hydrogen will appear at the cathode instead of sodium (p. 324) while chlorine will be evolved at the anode, as before. The reason why hydrogen is evolved from the cathode may be said to be that the sodium at first liberated by the electrolysis attacks the water forming NaOH and liberating hydrogen. As this reaction is exothermic, viz., $Na + HOH = NaOH + H + 43{,}500$, the amount of electrical energy necessary to electrolyse the aqueous solution is less than that required for the fused salt by the equivalent of this amount of heat. Caustic soda being the product required, not sodium, which when obtained must be treated with water to make the caustic, it would seem preferable to electrolyse a solution of salt rather than the fused material.

When fused salt is electrolysed the sodium must be collected in some solvent for it, such as metallic lead, which is heavier than the liquid salt; otherwise the sodium would float to the surface and burn in the air or chlorine there present. The cathode, therefore, consists of melted lead at the bottom of the crucible (of iron lined with magnesia) containing the melted salt, and the anode is a carbon rod immersed in the molten mass. Sodium is liberated at the cathode and dissolves in the melted lead, whilst chlorine is evolved at the anode and is led away from the top of the crucible to a bleaching-powder chamber (p. 183). The alloy of sodium and lead is treated with water to convert the Na into NaOH.

Instead of using a lead cathode the fused salt may contain lead chloride, so that the alloy of lead and sodium is separated electrolytically at the carbon cathode and sinks in the liquid salt.

When a solution of salt is electrolysed, the caustic soda collecting in solution around the cathode is liable to mix with the saturated solution of chlorine collect-

ing around the anode, forming a solution of sodium of hypochlorite and chloride (p. 182), which has powerful bleaching properties (*electrolytic bleach*). When the anode and cathode are separated by a porous diaphragm the caustic soda liquor may be drawn off and evaporated, whilst the chlorine may be conducted into lime chambers. The diaphragm constitutes a serious difficulty in the process, as a material which will satisfactorily resist the disintegrating effect of the electrolysis does not exist. In the *Castner-Kellner* process the anode and cathode are separated by a non-porous (and therefore less easily attacked) partition, which dips into a layer of mercury; in the anode compartment the mercury dissolves sodium, and by rocking the vessel is made to flow to the cathode compartment where its sodium is dissolved as caustic soda. Thus the vessel being continually rocked, the mercury serves to convey the sodium from anode to cathode without allowing the liquids in the compartments to mix.

184. **Sodium.**—Potash and soda exhibit so much similarity in their properties that we cannot be surprised at their having been confounded together by the earlier chemists, and it was not till 1736 that Du Hamel pointed out the difference between them. The discovery of potassium naturally led Davy to that of sodium, which can be obtained by processes exactly similar to those adopted for procuring potassium, to which it will be remembered sodium presents very great similarity in properties (p. 20). Sodium, however, is readily distinguished from potassium by its burning with a yellow flame, which serves even to characterise it when in combination.

This yellow flame is well seen by dissolving salt in water in a plate, and adding enough alcohol to render it inflammable, the mixture being well stirred while burning. A little piece of sodium burnt in an iron spoon held in a flame tinges yellow all the flames in the room, even at a remote distance. The blowpipe flame may also be employed to detect sodium by this colour, as in the case of potassium (p. 335). In fireworks, sodium nitrate is used for producing yellow flames. A very good *yellow fire* may be made by carefully and intimately mixing, in a mortar, 74 grains of nitrate of soda, 20 grains of sulphur, 6 grains of sulphide of antimony, and 2 grains of charcoal, all carefully dried, and very finely powdered.

Sodium is manufactured by electrolysing fused caustic soda in an iron vessel kept hot by a suitable furnace. Sodium and hydrogen are separated at the cathode and oxygen at the anode.

The iron cathode is surrounded by iron wire gauze terminating at the surface of the liquid in an inverted pot in which the sodium and hydrogen collect as they rise through the liquid. The anode is an iron cylinder surrounding the gauze. The object of the latter is really that of a porous diaphragm to keep the cathode and anode products apart; the reason why a material with such large pores can be used is because the fused sodium has a high surface tension and will not pass through the gauze. When sufficient sodium has collected in the inverted pot, the bottom of this is removed and the metal ladled out.

Sodium is a whiter metal than potassium; its sp. gr. is 0.973; it melts at 95°.6 C., and boils at 742° C. When heated in air, it gives a mixture of Na_2O and Na_2O_2, which is converted into NaOH by water, O being evolved from the Na_2O_2. If water be gradually added to Na_2O_2, it dissolves, and the solution yields crystals of $Na_2O_2.8H_2O$.

Sodium is not attacked by perfectly dry chlorine, dry bromine, or dry oxygen, but if a trace of aqueous vapour be present, combination occurs with violence. When mixed with 10 to 30 per cent. of its weight of potassium, sodium yields an alloy which is liquid at temperatures above 0° C. and is used for filling thermometers.

Sodium is far less costly than potassium, and is used on the large scale for making sodium peroxide. An amalgam of sodium (p. 85) is

also employed with advantage in extracting gold and silver from their ores.

Sodium hydride is similar to the potassium compound (p. 335).

Sodium peroxide, Na_2O_2, is manufactured by causing slices of sodium, disposed on trays of aluminium (which is not attacked), to pass through a hot (400° C.) tunnel which is traversed in the contrary direction by a current of dry air, freed from CO_2. It is a yellowish-white powder much used as an oxidising and bleaching agent.

Sodium chloride, NaCl, forms rock salt and *table salt*, the latter consisting of minute crystals formed by boiling down the water of brine springs (see p. 343). It forms cubical, anhydrous crystals of sp. gr. 2.15, and is almost equally soluble in hot and cold water; 100 parts of water at 15° C. dissolve 36 parts of salt, at 100° 39 parts. It is insoluble in alcohol. It melts at 772° C., and is afterwards vaporised. It forms two *cryohydrates*, NaCl.2Aq, deposited from a saturated solution cooled to − 10° C., and NaCl.10Aq, deposited at − 22° C. They are decomposed at higher temperatures. Needles of NaCl.2Aq are obtained from a solution of salt in hot HCl.

Sodium fluoride, NaF, made by fusing fluor spar (CaF_2) with Na_2CO_3, is used for softening boiler feed waters.

The *sulphides of sodium* are similar to those of potassium.

Sodium sulphate is found anhydrous as *Thénardite*. *Glauber's salt*, $Na_2SO_4.10Aq$, is made by crystallising salt cake. It forms prismatic crystals which effloresce in air, fuse at 33° C., and becomes anhydrous at 100°. It is more soluble in water at 33° C. than at any other temperature, 100 parts of water dissolving 115 parts of the crystals. When this solution is heated, it deposits anhydrous, Na_2SO_4, the temperature, 33° C., being the transition-point (p. 315) between the hydrate and the anhydrous salt. When cooled quietly in a covered vessel, the solution exhibits, in a high degree, the phenomenon of *supersaturation* (p. 50), and when the supersaturated solution is cooled to 5° C. crystals of $Na_2SO_4.7Aq$ may be obtained. The crystals of $Na_2SO_4.10Aq$, with half their weight of strong HCl, form an excellent freezing-mixture, giving the same temperature as ice and salt (− 18° C., 0° F.)—

$$Na_2SO_4.10Aq + HCl = NaHSO_4 + NaCl + 10Aq.$$

Anhydrous Na_2SO_4 melts at 865° C.; the double salt $Na_2SO_4K_2SO_4$ crystallises in plates (*plate sulphate*) from hot water, a flash of light accompanying the separation of each crystal.

Glauberite is $Na_2Ca(SO_4)_2$, and is nearly insoluble in water.

Hydrogen sodium sulphate, $NaHSO_4$, or *bisulphate of soda*, crystallises in prisms with 1Aq. It is more fusible and more easily decomposed by heat than is $KHSO_4$. It is decomposed by alcohol into H_2SO_4, and Na_2SO_4, which remains undissolved. When moderately heated, $2NaHSO_4 = H_2O + Na_2S_2O_7$ (*pyrosulphate*), decomposed by a red heat into Na_2SO_4 and SO_3. Sodium pyrosulphate is also formed when NaCl is heated with SO_3; $2NaCl + 3SO_3 = Na_2S_2O_7 + SO_2Cl_2$.

Sodium sulphite crystallises in prisms, $Na_2SO_3.7Aq$, which are very soluble in water, yielding an alkaline solution. It is prepared by saturating one-half of a solution of Na_2CO_3 with SO_2 gas, and adding the other half—

$$(1)\ Na_2CO_3 + 2SO_2 + H_2O = 2NaHSO_3 + CO_2;$$
$$(2)\ 2NaHSO_3 + Na_2CO_3 = 2Na_2SO_3 + H_2O + CO_2.$$

The sodium sulphite is useful in the laboratory as a reducing-agent (p. 221), and the *hydrogen sodium sulphite* (*bisulphite*), $NaHSO_3$, is used in organic chemistry and by the brewer.

Sodium thiosulphate, $Na_2S_2O_3$, or *hyposulphite of soda*, crystallises in glassy prisms, $Na_2S_2O_3.5Aq$, the preparation and properties of which have been described at p. 235.

Sodium thiosulphate is much used in photography for fixing prints by dissolving the unaltered portion of the sensitive film of silver chloride, bromide, or iodide. It is also used by bleachers as an *antichlore*.

Phosphate of soda, or *hydrogen disodium phosphate*, HNa_2PO_4, crystallises in prisms, $Na_2HPO_4.12Aq$, which effloresce in air and dissolve easily in water, giving an alkaline solution. When heated, they fuse easily, and lose the 12Aq at 45° C.; at a red heat, $2Na_2HPO_4 = H_2O + Na_4P_2O_7$ (*pyrophosphate*).

Na_2HPO_4 occurs in the blood and in urine. It is prepared by decomposing a mineral phosphate, which contains $Ca_3(PO_4)_2$, with H_2SO_4, so as to obtain the insoluble $CaSO_4$ and a solution of impure H_3PO_4. This is decomposed by Na_2CO_3, the solution filtered from the small quantity of $CaCO_3$, evaporated and crystallised—

$$H_3PO_4 + Na_2CO_3 = Na_2HPO_4 + H_2O + CO_2.$$

Arsenate of soda, or *hydrogen disodium arsenate*, HNa_2AsO_4, forms crystals with 12Aq, resembling those of the phosphate, but the salt as commonly sold contains 7Aq. There exists also the salt $Na_2HPO_4.7Aq$, but this is not that commonly sold.

Sodium arsenate is made by dissolving white arsenic in caustic soda, adding sodium nitrate, evaporating to dryness, heating the residue to redness and dissolving in water—

$$(1)\ As_4O_6 + 12NaOH = 4Na_3AsO_3 + 6H_2O;$$
$$(2)\ Na_3AsO_3 + NaNO_3 = Na_3AsO_4 + NaNO_2;$$
$$(3)\ Na_3AsO_4 + H_2O = Na_2HAsO_4 + NaOH.$$

185. **Borax**, *biborate of soda* ($Na_2O.2B_2O_3$), or *sodium pyroborate* ($Na_2B_4O_7$).—It has already been stated that borax is deposited during the evaporation of the waters of certain lakes in Thibet, whence it is imported into this country in impure crystals (*tincal*), which are covered with a peculiar greasy coating. Borax has also been found abundantly in Southern California.

The refiner of tincal powders the crystals and washes them, upon a strainer, with a weak solution of soda, which converts the greasy matter into a soap and dissolves it. The borax is then dissolved in water, a quantity of sodium carbonate is added to separate some lime which the borax usually contains, and, after filtering off the carbonate of lime, the solution is evaporated to the crystallising point and allowed to cool, in order that it may deposit the pure crystals of borax. *Boracite*, $2CaO.3B_2O_3$, from Asia Minor, is frequently used as a raw material for making borax; the mineral is boiled with Na_2CO_3, the $CaCO_3$ filtered, and the solution crystallised.

Borax is manufactured in this country by heating sodium carbonate with boric acid, when the latter expels the carbonic acid.* The mass is then dissolved in water, and the borax crystallised, an operation upon which much care is bestowed, since the product does not meet with a ready sale unless in large crystals. The solution of borax, having been evaporated to the requisite degree of concentration, is allowed to crystallise in covered wooden boxes, which are lined with lead and

* The ammonia which is evolved from the Tuscan boracic acid employed in this process is known in commerce as *Volcanic ammonia*, and is free from the empyreumatic odour which generally accompanies that from coal and bones.

enclosed in an outer case of wood, the space between the sides of the case and the box being stuffed with some bad conductor of heat, so that the solution of borax may cool very slowly, and large crystals may be deposited. In about thirty hours the crystallisation is completed, when the liquid is drawn off as rapidly as possible, the last portion being carefully soaked up with sponges, so that no small crystals may be afterwards formed upon the surface of the large ones; the case is then again covered up, so that the crystals may cool slowly without cracking. When a solution of borax is crystallised above 56° C., it yields *octahedral borax*, $Na_2B_4O_7.5Aq$. which is also deposited when solution of prismatic borax is evaporated *in vacuo*.

The ordinary prismatic crystals of borax are represented by the formula $Na_2B_4O_7.10Aq$. They soon effloresce and become opaque when exposed to air, and may readily be distinguished by their alkaline taste and action upon test-papers, and especially by their behaviour when heated, for they fuse easily and *intumesce* most violently, swelling up to a white spongy mass of many times their original bulk; this mass afterwards fuses down to a clear liquid which forms a transparent glassy mass on cooling (*vitrefied borax*), and since this glass is capable of dissolving many metallic oxides with great readiness (borax being, by constitution, an acid salt, and therefore ready to combine with more base), it is much used in the metallurgic arts. Large quantities of borax are also employed in glazing stoneware.

A dilute solution of borax dissolves iodine to a colourless solution, but on concentration the iodine is precipitated; probably the borax is decomposed in the dilute solution into boric acid and soda, which converts the iodine into iodide and iodate: on concentrating, the boric acid liberates hydriodic and iodic acids, which react with each other, separating iodine (p. 200).

Sodium nitrate or *nitrate of soda*, $NaNO_3$, also known as *Peruvian Chili saltpetre*, is found in Peru and Chili in beds beneath the surface soil, where it is dug out and crystallised from water. It is often spoken of as *cubical saltpetre*, since it crystallises in rhombohedra, easily mistaken for cubes, whilst *prismatic saltpetre*, nitrate of potassium, crystallises in six-sided prisms. Sodium nitrate cannot be substituted for potassium nitrate as an ingredient of gunpowder, since it attracts moisture from the air, becoming damp, and is less powerful in its oxidising action upon combustible bodies at a high temperature. It is, however, used for making potassium nitrate for gunpowder (p. 337). A much more extended application is its use as a manure, for supplying nitrogen; large quantities are also used for making nitric acid. It melts at 320° C. and dissolves in water to the extent of 87 per cent. at 20° C. and 180 per cent. at 100° C.

Sodium nitrite, $NaNO_2$, is much used for diazotising organic amides (p. 106). It is made by heating $NaNO_3$ to 420° C. in an iron vessel and stirring the molten mass with metallic lead; $NaNO_3 + Pb = NaNO_2 + PbO$. It crystallises in colourless deliquescent prisms very soluble in water; the solution of the commercial salt is generally alkaline owing to the presence of a small quantity of caustic soda, but the pure salt is neutral.

Sodium silicate.—A combination of soda with silica has long been used, under the name of *soluble glass*, for imparting a fire-proof character to wood and other materials, and, more recently, for producing artificial stone for building purposes, and for a peculiar kind of permanent fresco-painting (*stereochromy*), the results of which are intended to withstand exposure to the weather.

Sodium metasilicate has been obtained in prismatic crystals, $Na_2SiO_3.8Aq$, by

dissolving amorphous silica in NaOH. It is soluble in water, and the solution is decomposed by CO_2. A solution of amorphous SiO_2 in hot aqueous Na_2CO_3 gelatinises, on cooling.

Soluble glass is usually prepared by fusing 15 parts of sand with 8 parts of carbonate of soda and 1 part of charcoal. The silicic acid, combining with the soda, disengages the carbonic acid gas, the expulsion of which is facilitated by the presence of charcoal, which converts it into carbonic oxide. The mass thus formed is scarcely affected by cold water, but dissolves when boiled with water, yielding a strongly alkaline liquid.

In using this substance for rendering wood fire-proof, a rather weak solution is first applied to the wood, and over this a coating of lime-wash is laid ; a second coating of soluble glass (in a more concentrated solution) is then applied. The wood so prepared is, of course, charred, as usual, by the application of heat, but its inflammability is remarkably diminished.

For the manufacture of *Ransome's artificial stone*, the soluble glass is prepared by heating flints, under pressure, with a strong solution of caustic soda, to a temperature between 300° and 400° F. (149° and 204° C.), when the silica constituting the flint enters into combination with the soda. Finely divided sand is moistened with this solution, pressed into moulds, dried, and exposed to a high temperature, when the silicate of soda fuses and cements the grains of sand together into a mass of artificial sandstone, to which any required colour may be imparted by mixing metallic oxides with the sand before it is moulded.

Silicate of soda is also sometimes used as a *dung substitute* in calico-printing (*q.v.*).

Sodium chlorate, $NaClO_3$, resembles the potassium salt, but is very soluble, and is on this account preferred for some purposes. It is made by substituting Na_2SO_4 for KCl in the method described on p. 184 for making $KClO_3$.

SALTS OF AMMONIUM.

186. The great chemical resemblance between some of the salts formed by neutralising acids with ammonia, and the salts of potassium and sodium, has been already pointed out as affording a reason for the hypothesis of the existence of a compound metal, *ammonium* (NH_4), equivalent in its functions to potassium and sodium (p. 85).

The compounds which are formed when ammonia (NH_3) combines with the anhydrides, such as carbonic (CO_2) and sulphuric (SO_3), do not exhibit the resemblance to the salts of potassium and sodium until water is added. Thus, by the action of dry ammonia gas upon sulphuric anhydride, a compound called *sulphuric ammonide* is formed, having the composition $(NH_3)_2SO_3$. This substance dissolves in water and crystallises in octahedra, but its solution is not precipitated by barium chloride, which always precipitates the true sulphates, nor by platinic chloride, which precipitates the true ammonium salts. By long boiling with water, however, it becomes ammonium sulphate, $(NH_4)_2SO_4$, which yields precipitates with both the above tests.* The phosphoric, carbonic, and sulphurous anhydrides also combine with nearly dry ammonia to form ammonides, which do not respond to the ordinary tests for the corresponding salts of ammonium until after water has been assimilated. The true salts of ammonium are produced either by the combination of an acid with ammonia, or by double decomposition.

Ammonium nitrate, NH_4NO_3, is prepared by neutralising ordinary nitric acid with lumps of ammonium carbonate, when the nitrate crystallises on cooling in six-sided prisms like those of KNO_3, but they are deliquescent and very soluble in water ; it absorbs one-third of its

* Representing sulphuric acid as sulphuryl hydroxide, $SO_2.OH.OH$, ammonium sulphate is $SO_2.ONH_4.ONH_4$, and sulphuric ammonide is $SO_2.NH_2.ONH_4$, the amidogen group, NH_2, being substituted for the ammon-oxyl group, $O(NH_4)$.

weight of ammonia and becomes liquid, the ammonia being expelled again at 25° C. When gently heated, it melts at 150° C., and is decomposed at 210° C., when it boils and passes off entirely as water and nitrous oxide; $NH_4NO_3 = 2H_2O + N_2O$. If sharply heated, as by throwing it on a red-hot surface, it deflagrates. If very carefully heated, it may be sublimed. It is largely used for making nitrous oxide, and is a constituent of some explosives.*

Ammonium nitrite, NH_4NO_2, is interesting on account of its easy decomposition by heat; $NH_4NO_2 = N_2 + 2H_2O$. This occurs even on boiling the solution, so that a mixture of solutions of potassium nitrite and ammonium chloride is used for preparing nitrogen. Ammonium nitrite is found, in very small quantity, in rain water; it can also be detected in the water condensed from hydrogen burning in air. Ammonia is partly converted into this salt when oxidised by ozone or even by air in presence of heated platinum; $2NH_3 + O_3 = NH_4NO_2 + H_2O$.

187. **Ammonium sulphate**, $(NH_4)_2SO_4$, is largely employed in the preparation of ammonia alum, and as an artificial manure, for which purposes it is generally obtained from the ammoniacal liquor of the gas-works by distillation with lime and absorption of the liberated ammonia in H_2SO_4. The rough crystals are gently heated to expel tarry substances, and purified by recrystallisation. The crystals have the same shape as those of potassium sulphate, and are easily soluble in water, but not in alcohol. When heated to about 260° C., the $(NH_4)_2SO_4$ is decomposed, yielding vapour of ammonium sulphite, water, ammonia, nitrogen, and sulphur dioxide. If muslin be dipped into a solution of ammonium sulphate in ten parts of water and dried, it will no longer burn with flame when ignited. The mineral *mascagnine* consists of ammonium sulphate. This salt is occasionally found in needle-like crystals upon the windows of rooms in which coal gas is burnt.

188. **Ammonium carbonate**, also called *smelling salts*, or *Preston salts*, is largely used in medicine, and by bakers and confectioners, for imparting lightness or porosity to cakes, &c. It is commonly prepared by mixing ammonium sulphate with twice its weight of chalk, and distilling the mixture in an earthern or iron retort, communicating, through an iron pipe, with a leaden chamber or receiver, in which the ammonium carbonate collects as a transparent fibrous mass, which is extracted by taking the receiver to pieces, and purified by resubliming it in iron vessels surmounted by leaden domes. The action of calcium carbonate upon ammonium sulphate would be expected to furnish the normal carbonate, $(NH_4)_2CO_3$, but this salt (even if produced) is decomposed by the heat employed in the process into *hydrogen ammonium carbonate*, $CO(ONH_4)(ONH_4) = CO(ONH_4)(OH) + NH_3$, and *ammonium carbamate*, $CO(ONH_4)(ONH_4) = CO(ONH_4)(NH_2) + H_2O$.

The commercial carbonate is usually a mixture of 2 mols. of the former to one of the latter. By treating it with strong alcohol, the carbamate is dissolved and the hydrogen ammonium carbonate left.

When exposed to the air it smells of ammonia, and gradually becomes NH_4HCO_3 or $CO(ONH_4)(OH)$, the carbamate being decomposed and volatilised; $CO(ONH_4)(NH_2) = CO_2 + 2NH_3$. On treating the commercial carbonate with a little water, the NH_4HCO_3 is left un-

* The explosive *Bellite* consists of 5 parts of ammonium nitrate and 1 part of di-nitro-benzene (*q.v.*); it is said to be 30 per cent. stronger than dynamite, and to explode only by detonation.

dissolved, whilst the carbamate is converted into normal carbonate and dissolved; $CO(ONH_4)(NH_2) + H_2O = (NH_4)_2CO_3$.

Sal volatile is an alcoholic solution of ammonium carbonate and carbamate.

By saturating ammonia solution with CO_2, crystals of *ammonium sesquicarbonate*, $(NH_4)_2CO_3.2NH_4HCO_3$ are obtained.

Ammonium carbonate, $(NH_4)_2CO_3$, is obtained in crystals by treating the commercial carbonate with strong ammonia. The crystals contain 1Aq. They are deliquescent in air, and evolve NH_3, becoming converted into the bicarbonate; $(NH_4)_2CO_3 = NH_3 + NH_4HCO_3$.

Ammonium bicarbonate, NH_4HCO_3 or hydrogen ammonium carbonate, is the most stable, and is obtained by dissolving the commercial carbonate in a little boiling water, when it crystallises on cooling.

The *ammonium carbamate* is deposited as a white solid when ammonia gas is mixed with carbonic acid gas, unless both be quite dry. It may be obtained in crystals by passing CO_2 and NH_3 into the strongest solution of ammonia.

Ammonium carbamate is easily soluble in water, which soon converts it into ammonium carbonate. The aqueous solution, when freshly prepared, is not precipitated by calcium chloride, but the calcium carbonate is deposited on standing or heating. When ammonium carbamate is heated in a sealed tube at 130° C. it is decomposed into ammonium carbonate and urea; $2NH_4CO_2NH_2 = (NH_4)_2CO_3 + CON_2H_4$. Carbamic acid, HCO_2NH_2, has not been isolated; its relation to carbonic acid is seen by a comparison of their formulæ; carbonic acid, CO.OH.OH: carbamic acid, $CO.OH.NH_2$. Other carbamates have been obtained by passing CO_2 through strongly ammoniacal solutions of different bases, and precipitating the carbamates by alcohol. When potassium carbamate is heated, it yields water and potassium cyanate; $KCO_2NH_2 = KCNO + H_2O$.

Carbamates are remarkable for evolving nitrogen when treated with a mixture of soda and sodium hypobromite, but *not with the hypochlorite;* thus—

$2(CO.NH_2.ONa) + 3NaOBr + 2NaOH = 2CO(ONa)_2 + 3NaBr + 3H_2O + N_2$.

If solution of sodium carbamate be mixed with sodium hypochlorite and soda, no nitrogen is evolved until a soluble bromide is added, a reaction which will indicate bromides even in dilute solutions. The solution of sodium carbamate may be prepared by dissolving ammonium carbamate in a strong solution of soda, and evaporating over strong sulphuric acid.

189. **Ammonium chloride** (NH_4Cl), also called *muriate of ammonia* and *sal ammoniac*.—When ordinarily dry NH_3 is brought in contact with an equal volume of dry HCl, it has been seen (p. 84) that they combine directly to produce this salt, the preparation of which on the large scale has been noticed at p. 78. Its commercial form is that of a very tough translucent fibrous mass, generally of the dome-like shape of the receivers in which it has been condensed, and often striped with brown, from the presence of a little iron. It has not the least smell of ammonia, and is very soluble in water, requiring about three parts of cold water, and little more than its own weight of boiling water. As the hot solution cools, it deposits beautiful fern-like crystallisations composed of minute cubes and octahedra. The dissolution of sal ammoniac in water lowers the temperature very considerably, which renders the salt very useful in freezing-mixtures. A mixture of equal weights of sal ammoniac and nitre, dissolved in its own weight of water, lowers the temperature of the latter from 10° to −12° C. In this case partial decomposition occurs, resulting in the production of potassium chloride and ammonium nitrite, both of which absorb much heat whilst being dissolved by water. The solution of ammonium chloride in water is slightly acid to blue litmus-paper. When sal ammoniac is heated, it vaporises, at a temperature below redness, without fusing; the vapour forms thick white clouds in the

air, and may be condensed as a white crust upon a cold surface; but it is said that it cannot be sublimed without some loss, a portion being decomposed into HCl, H and N.

As already stated (p. 85), ammonium chloride dissociates when heated, so that the heat which becomes latent or is *absorbed* in vaporising the NH_4Cl, is almost exactly that which is *produced* by the combination of the hydrochloric acid and ammonia, viz., NH_3, $HCl = 42{,}000$.

When ammonium chloride is heated with metallic oxides, the hydrochloric acid often converts the oxide into a chloride which is either fusible or volatile, so that sal ammoniac is often employed for cleansing the surfaces of metals previously to soldering them. Even those metallic oxides which are destitute of basic properties, such as antimonic and stannic oxides, are convertible into chlorides by the action of sal ammoniac at a high temperature.

Ammonium chloride is found in volcanic districts, and is present in very small quantity in sea water.

190. *Hydrosulphate of ammonia*, $2NH_3.H_2S$, or **ammonium sulphide**, $(NH_4)_2S$, has been obtained in colourless crystals by mixing hydrosulphuric acid gas with twice its volume of ammonia gas in a vessel cooled by a mixture of ice and salt.* It is a very unstable compound, decomposing in solution into free ammonia and *ammonium hydrosulphide*, NH_4HS, which may also be obtained in solution by saturating with H_2S at 0° C. strong ammonia diluted with four times its volume of water.

Solution of ammonium sulphide, prepared by mixing the "hydrosulphide" (made by saturating ammonia solution with H_2S) with an equal volume of ammonia, is much used in analytical chemistry, and is supposed to contain $(NH_4)_2S$. The solution has a very disagreeable odour.

When a strong solution of ammonia is saturated with hydrogen sulphide at 0° C., a colourless solution is formed, from which colourless crystals separate, the composition of which varies with the strength of the ammonia, but may be expressed by the general formula, $(NH_4)_2S.xNH_4HS$. The solution soon becomes yellow in contact with the air, from the formation of *ammonium polysulphides* of the form $(NH_4)_2S_x$; eventually the solution deposits sulphur and becomes colourless, thiosulphate, sulphite, and sulphate of ammonium being formed. When the freshly prepared colourless solution is mixed with an acid, the solution remains clear, H_2S being evolved with effervescence; $NH_4HS + HCl = NH_4Cl + H_2S$ and $(NH_4)_2S + 2HCl = 2NH_4Cl + H_2S$; but if the solution be yellow, a milky precipitate of sulphur is produced, from the decomposition of the polysulphides; $(NH_4)_2S_x + 2HCl = 2NH_4Cl + H_2S + S_{x-1}$.

The fresh solution gives a black precipitate of lead sulphide when solution of lead acetate is added to it, but after it has been kept till it is of a dark yellow or red colour, it gives a red precipitate of the persulphide of lead.

Ammonium polysulphides are the chief constituents of *Boyle's fuming liquor*, a fetid yellow liquid obtained by distilling sal ammoniac with sulphur and lime. They are sometimes deposited in yellow crystals from this liquid. By dissolving sulphur in ammonium disulphide, orange-yellow prismatic crystals of *ammonium pentasulphide*, $(NH_4)_2S_5$, may be obtained.

Ammonium bromide (NH_4Br) and *ammonium iodide* (NH_4I) are useful in photography. They are both colourless crystalline salts, but the iodide is very liable to become yellow or brown, from the separation of iodine, unless kept dry and in the dark. Both salts are extremely soluble in water.

Microcosmic salt, *phosphorus salt*, or *hydrogen sodium ammonium phosphate*, $HNaNH_4PO_4.4Aq$, is found in putrid urine and in guano. It is prepared by mixing hot strong solutions of ammonium chloride and sodium phosphate—

$$Na_2HPO_4 + NH_4Cl = HNaNH_4PO_4 + NaCl.$$

* When the NH_3 is in large excess a volatile liquid, $(NH_4)_2S.2NH_3$, is formed, the vapour of which is very poisonous.

It forms prismatic crystals which are very soluble and fusible, boiling violently when further heated, and finally leaving a transparent glass of sodium metaphosphate, which is valuable in blowpipe work for dissolving metallic oxides; $NaNH_4HPO_4 = NH_3 + H_2O + NaPO_3$.

LITHIUM.

Li = 7 parts by weight.

191. This comparatively rare metal is obtained chiefly from the minerals *lepidolite* (λεπὶς, *a scale*) or *lithia-mica*, containing silicate of alumina with fluorides of potassium and lithium; *petalite* (πέταλον, *a leaf*), silicate of soda, lithia, and alumina; and *triphane* or *spodumene* (σποδὸς, *ashes*), which has a similar composition. Its name (from λίθος, *a stone*) was bestowed in the belief that it existed only in the mineral kingdom, but recent investigation has detected it in minute proportion in the ashes of tobacco and other plants. The water of a hot spring in Clifford United Mines, in Cornwall, contains 26 grains of lithium chloride per gallon.

Metallic lithium is obtained by decomposing fused lithium chloride by a galvanic current. It is remarkable as the lightest solid known (sp. gr. 0.59). It bears a general resemblance to potassium and sodium, but it is harder and less easily oxidised than those metals. It decomposes water rapidly at the ordinary temperature, but does not inflame upon it. It melts at 186° C., but cannot be distilled.

Lithium bears some resemblance to calcium as well as to potassium and sodium. Thus it forms an *oxide*, Li_2O, when it burns, which is earthy, and dissolves only gradually in water, unlike oxides of K and Na. The *hydroxide* LiOH, obtained by causticising the carbonate with lime, is less soluble than KOH and NaOH and a less powerful alkali. Another leaning towards the calcium group of metals is seen in the sparing solubility of lithium *phosphate*, Li_3PO_4 (1 in 2500), and *carbonate*, Li_2CO_3 (1 in 100). The latter, however, is not decomposed by heat as calcium carbonate is; it is made from lepidolite by fusing the mineral, powdering it, boiling with HCl and HNO_3 and precipitating the iron lime, &c., by Na_2CO_3; the filtrate contains NaCl, KCl, and LiCl; it is concentrated and mixed with Na_2CO_3 to precipitate the Li_2CO_3.

The "lithia" used as a remedy for gout is a mixture of lithium carbonate and citric acid, the latter dissolving the former as lithium citrate with effervescence when the mixture is put in water.

The compounds of lithium impart a red colour to a flame.

RUBIDIUM AND CÆSIUM.

Rb′ = 84.8 parts by weight, Cs′ = 132 parts by weight.

192. These elements were discovered in 1860, by Bunsen and Kirchhoff, during the analysis of a certain spring water which contained these metals in so minute quantity (2 or 3 grains in a ton) that they would certainly have escaped observation if the analysis had been conducted in the ordinary way. The discovery of these metals, as well as of three others (thallium, indium, gallium), to be mentioned hereafter, was the result of the application of the method of *spectrum analysis* (see p. 329).

When examining, with the spectroscope, the alkali chlorides extracted from the spring water, Bunsen and Kirchhoff observed two red and two blue bands in the spectrum, which they could not ascribe to any known substance, and which they ultimately traced to the two new metals, rubidium (*rubidus*, dark-red) and cæsium (*cæsius*, sky-blue), which may be isolated by the electrolysis of their fused salts, or by distilling them from a mixture of their hydroxides with magnesium.

Rubidium (m. p. 38°; sp. gr. 1.52) has since been found in small quantity in carnallite, in lepidolite, and in the ashes of many plants. This metal is closely related in properties to potassium, but is more easily fusible and convertible into vapour, and actually surpasses that metal in its attraction for oxygen, rubidium taking fire spontaneously in air, forming RbO_2. It burns on water with exactly the same flame as potassium. Its hydroxide is a powerful alkali, like potash, and its salts are isomorphous with, and more soluble than, those of potassium. The double chloride of platinum and potassium is eight times as soluble in boiling water as the corresponding salt of rubidium, which is taken advantage of in separating these two allied metals. Rubidium forms stable and sparingly soluble double salts

with many halides; thus the borofluoride, $RbBF_4$, requires 100 parts of boiling water to dissolve it.

Cæsium (m. p. 27°; sp. gr. 1.88) appears to be even more highly electro-positive than rubidium, forming a strong alkali, cæsium hydroxide, and salts which are isomorphous with those of potassium. Cæsium carbonate, however, is soluble in alcohol, which does not dissolve the carbonates of potassium and rubidium. Moreover, the cæsium bitartrate is nine times as soluble in water as the rubidium bitartrate is.

Cæsium has been found in lepidolite; and the rare mineral *pollux*, found in Elba, and resembling felspar in composition, is said to contain a very large quantity of this metal. The alum of the island of Vulcano is mentioned as a rich source of cæsium and rubidium.

Metallic cæsium cannot be obtained by reduction with carbon, but it has been extracted by decomposing its cyanide by the galvanic current.

Both rubidium and cæsium show a remarkable tendency to combine with halogens as though they were trivalent or pentavalent, forming such compounds as $RbICl_4$, CsI_3, and $RbIBr_2$.

193. **General review of the group of alkali metals.**—Cæsium, rubidium, potassium, sodium, and lithium constitute a group of elements conspicuous for their highly electro-positive character, the powerfully alkaline nature of their hydroxides, and the general solubility of their salts. Their chemical characters and functions are directly opposite to those of the electro-negative group containing fluorine, chlorine, bromine, and iodine, and, like those elements, they exhibit a gradation of properties. Thus, cæsium appears to be the most highly electro-positive member, rubidium the next, then potassium and sodium, whilst lithium is the least electro-positive; and just as iodine, the least electro-negative of the halogens, possesses the highest atomic number, so cæsium, the least electro-negative (or most electro-positive) of the alkali-metals, has a higher atomic weight than any other member of this group, their atomic weights being represented by the numbers, cæsium, 132; rubidium, 85; potassium, 39; sodium, 23; lithium, 7. As in the case of the halogens, also, these are all monovalent elements. Just as chlorine is accepted as the representative of *chlorous radicles*, so potassium is commonly regarded as the type of *basylous radicles*, the term radicle being applied to all substances, whether elementary or compound, which are capable of being transferred, like chlorine or potassium, from one compound to another without suffering decomposition.

Attention has been called (p. 304) to the gradation exhibited in some of the physical properties of these elements.

In some of their salts a similar gradational relation is observed; the carbonates, for example, of cæsium, rubidium, and potassium are highly deliquescent, absorbing water greedily from the air, while carbonate of sodium is not deliquescent, and carbonate of lithium is sparingly soluble in water. The difficult solubility of the carbonate and phosphate of lithium constitutes the connecting link between this and the succeeding group of metals, the carbonates and phosphates of which are insoluble in water.

BARIUM.

$Ba'' = 136.4$ parts by weight.

194. **Barium**, so named from the great weight of its compounds (*βαρύς, heavy*), is found in considerable abundance in the north of England, in two minerals known as *Witherite* (barium carbonate, $BaCO_3$)

and *heavy spar* or *barytes* (barium sulphate, $BaSO_4$). Witherite is found in large masses in the lead mines at Alston Moor, and at Anglesark in Lancashire. It is said to be used for poisoning rats, and was originally mistaken, on account of its great weight (sp. gr. 4.5), for an ore of lead. All salts of barium are poisonous.

The metal itself is obtained by electrolysing fused barium chloride or heating it with sodium. It is a pale yellow malleable metal of sp. gr. 3.6; it is easily oxidised by air, and rapidly decomposes water at common temperatures. It requires a high temperature to fuse it. Barium and its salts impart a green colour to a flame.

Such compounds of barium as are used in the arts are chiefly prepared from heavy spar or barium sulphate, which is remarkable for its insolubility in water and acids. In order to prepare other compounds of barium from this refractory mineral, it is ground to powder and strongly heated in contact with charcoal or some other carbonaceous substance, which removes the oxygen from the mineral in the form of carbonic oxide, thus converting the barium sulphate into *barium sulphide*; $BaSO_4 + C_4 = 4CO + BaS$. This latter compound, being soluble in water, can be readily converted into other barium compounds.

The artificial *barium sulphate*, which is used by painters, instead of white lead, under the name of *permanent white* (*blanc fixe*), and is employed for glazing cards, is prepared by mixing the solution of barium sulphide with dilute sulphuric acid, when the barium sulphate separates as a white precipitate, which is collected, washed, and dried—

$$BaS + H_2SO_4 = H_2S + BaSO_4.$$

The artificial *barium carbonate*, which is used in the manufacture of some kinds of glass, is prepared by passing carbonic acid gas through a solution of barium sulphide, when the carbonate is precipitated; $BaS + H_2O + CO_2 = H_2S + BaCO_3$.

In preparing compounds of barium from heavy spar on the small scale it is better to convert the sulphate into barium carbonate. 50 parts of the finely powdered sulphate are mixed with 100 of dried sodium carbonate, 600 of powdered nitre, and 100 of very finely powdered charcoal. The mixture is placed in a heap upon a brick or iron plate, and kindled with a match, when the heat evolved by the combustion of the charcoal in the oxygen of the nitre fuses the barium sulphate with the sodium carbonate, whereupon they react to form barium carbonate and sodium sulphate: $BaSO_4 + Na_2CO_3 = Na_2SO_4 + BaCO_3$. The mass is thrown into boiling water, which dissolves the sodium sulphate and leaves the barium carbonate. The latter may be allowed to settle, and washed several times, by decantation, with distilled water, until the washings no longer yield a precipitate with barium chloride, showing that the whole of the sodium sulphate has been washed away and pure barium carbonate remains.

Barium oxide or *baryta*, BaO, may be obtained by strongly heating a mixture of barium carbonate and charcoal, $BaCO_3 + C = BaO + 2CO$, but is now generally prepared by heating the nitrate, $Ba(NO_3)_2 = BaO + 2NO_2 + O$. It is a heavy grey solid which combines with water with great evolution of heat to form barium hydroxide.

Barium dioxide or *peroxide*, BaO_2, has been noticed under hydrogen dioxide (p. 63) and under Brin's oxygen process (p. 39).

Barium hydroxide, $Ba(OH)_2$, may be prepared by passing CO_2 and steam over barium sulphide at a red heat, and decomposing the carbonate thus produced by a current of superheated steam: (1) $BaS + CO_2 + H_2O = BaCO_3 + H_2S$; (2) $BaCO_3 + H_2O = Ba(OH)_2 + CO_2$. It dissolves in boiling water, and crystallises in prisms, $Ba(OH)_2.8Aq$.

Crystallised barium hydroxide may be produced by adding 113 grams of powdered barium nitrate to 340 c.c. of a boiling solution of NaOH, containing 85 grams of commercial caustic soda in 567 c.c. of water; the solution becomes turbid from the separation of barium carbonate produced from the sodium carbonate in the hydroxide; it is boiled for some minutes and then filtered; on partial cooling, some crystals of undecomposed barium nitrate are deposited, and if the clear liquid be poured off into another vessel and stirred, it deposits abundant crystals of barium hydroxide having the composition $Ba(OH)_2.8Aq$; these effloresce and become opaque when exposed to air, becoming $Ba(OH)_2.Aq$; when heated to redness they become pure, $Ba(OH)_2$, which fuses, but is not decomposed when further heated. The hydroxide is moderately soluble in water (*baryta water*), 100 parts of water dissolving 3 parts at the ordinary temperature; the solution is strongly alkaline and absorbs carbonic acid gas from the air, depositing barium carbonate.

Barium carbonate, $BaCO_3$, or Witherite, has the sp. gr. 4.3. It may be prepared by precipitating barium chloride with sodium carbonate. It is very insoluble in water, and is not decomposed by a red heat.

Barium chloride, which is the barium compound most commonly employed in the laboratory, may be obtained by dissolving the carbonate in diluted hydrochloric acid, and evaporating the solution; on cooling, the chloride is deposited in tabular crystals, $BaCl_2.2Aq$.

On the large scale, it is generally manufactured by fusing heavy spar with calcium chloride (the residue from the preparation of ammonia, see p. 79) in a reverberatory furnace, $BaSO_4 + CaCl_2 = CaSO_4 + BaCl_2$. The mass is rapidly extracted with hot water, which leaves the calcium sulphate undissolved, and the clear solution of barium chloride is decanted and evaporated. If the calcium sulphate and barium chloride were allowed to remain long together in contact with the water, barium sulphate and calcium chloride would be reproduced. This process has been improved by adding chalk and coal-dust to the mixture, when (1) $BaSO_4 + C_4 = BaS + 4CO$; (2) $BaS + CaCl_2 = BaCl_2 + CaS$. The calcium sulphide forms an insoluble compound with the lime from the chalk.

Barium chloride is easily soluble in water, but insoluble in alcohol and in strong acids. *Barium bromide* is soluble in alcohol.

Barium nitrate, $Ba(NO_3)_2$, is obtained by dissolving the carbonate in dilute nitric acid, and evaporating the solution, when octahedral crystals of the nitrate are deposited. It is an ingredient in some kinds of blasting powder used by miners. When heated, it fuses and is decomposed, leaving a grey porous mass of baryta.

Barium chlorate, $Ba(ClO_3)_2$, is employed in the manufacture of fireworks, being prepared for that purpose by dissolving the artificial barium carbonate in solution of chloric acid; it forms beautiful shining tabular crystals. When mixed with combustible substances, such as charcoal and sulphur, it imparts a brilliant green colour to the flame of the burning mixture (see p. 186).

Barium sulphate, $BaSO_4$, found as heavy spar or *cawk*, has the sp. gr. 4.5. It is precipitated whenever sulphates and barium salts meet in solution. It is remarkable for its insolubility in water and acids, and is the form in which either barium or sulphur is determined in quantitative analysis. It dissolves in hot strong H_2SO_4, and the solution, on cooling, deposits crystals of *acid barium sulphate*, $BaH_2(SO_4)_2$.

Barium sulphide, BaS, prepared as described above, dissolves in water with decomposition, yielding barium hydroxide and sulphydrate; $2BaS + 2H_2O = Ba(OH)_2 + Ba(SH)_2$. It has the property of shining in the dark after it has been exposed to the action of light.

Barium carbide, BaC_2, is a grey amorphous substance made by heating $BaCO_3$ (26 parts) with magnesium powder (10.5 parts) and powdered coke (4 parts) in an iron flask; $BaCO_3 + Mg_3 + C = BaC_2 + 3MgO$. It evolves acetylene when treated with water, $BaC_2 + 2H_2O = C_2H_2 + Ba(OH)_2$.

STRONTIUM.

Sr″ = 87 parts by weight.

195. Strontium is less abundant than barium, and occurs in nature in similar forms of combination. *Strontianite*, the *strontium carbonate* ($SrCO_3$), was first discovered in the lead-mines of Strontian in Argyleshire, and has since been found in small quantity in some mineral waters. $SrCO_3$ is more easily dissociated by heat than is $BaCO_3$, but less easily than is $CaCO_3$.

Celestine (so called from the blue tint of many specimens*) is the *strontium sulphate* ($SrSO_4$), and is found in beautiful crystals associated with the native sulphur in Sicily. It is also met with in this country, and is the source from which the *strontium nitrate* employed in firework compositions is derived. The strontium sulphate resembles barium sulphate with respect to its insolubility, and is converted into the soluble *strontium sulphide* (SrS) by calcination with carbonaceous matter. The solution of strontium sulphide so obtained is decomposed by nitric acid, and the strontium nitrate crystallised from the solution. It has the property of imparting a magnificent crimson colour to flames, and is hence largely used for the preparation of red theatrical fire (see p. 186).

The metal itself is prepared in a similar manner to metallic barium,† which it much resembles, but is lighter (sp. gr. 2.54) and more fusible. It burns, when heated in air, with a crimson flame.

Strontia, SrO, resembles BaO, but does not absorb O when heated.

Strontium dioxide, SrO_2, is precipitated, in combination with $8H_2O$, when a solution of strontia in water is mixed with hydrogen peroxide.

Strontium hydroxide, $Sr(OH)_2$, is made on the large scale by heating the native strontium sulphate with brown iron ore (hydrated ferric oxide) and coal-dust. On treating the product with water, ferrous sulphide remains undissolved, and $Sr(HO)_2$ passes into solution. It is used in sugar refining. It is less soluble than barium hydroxide, and is converted into SrO by heat.

Strontium nitrate, $Sr(NO_3)_2$, may be prepared by dissolving strontianite in nitric acid. It crystallises from hot strong solutions in anhydrous octahedra. Cold solutions deposit prisms of $Sr(NO_3)_2.4Aq$. (Barium nitrate is always anhydrous.) Strontium nitrate is easily soluble in water, but insoluble in alcohol.

Strontium chloride, $SrCl_2$, differs from $BaCl_2$ in being deliquescent and soluble in alcohol. It crystallises in prisms, $SrCl_2.6Aq$.

Strontium sulphate, $SrSO_4$, is not so heavy as $BaSO_4$; sp. gr. 3. It is slightly soluble in water, and is easily converted into $SrCO_3$ by alkaline carbonates, in the cold, which is not the case with $BaSO_4$.

* Said to be due to the presence of ferroso-ferric phosphate.

† Strontium has been made in quantity by distilling strontium amalgam in hydrogen. The amalgam was prepared by the action of sodium-amalgam on a saturated solution of strontium chloride.

CALCIUM.

Ca″ = 40 parts by weight.

196. No other metal is so largely employed in a state of combination as is calcium, for its oxide, *lime* (CaO), occupies among bases much the same position as that which sulphuric acid holds among the acids, and is used, directly or indirectly, in most of the arts and manufactures.

Like barium and strontium, calcium is found, though far more abundantly than these, in the mineral kingdom, in the forms of carbonate and sulphate, but it also occurs in large quantity as calcium fluoride (p. 202), and less frequently in the form of phosphate (p. 256). Calcium, moreover, is found in all animals and vegetables, and its presence in their food, in one form or other, is an essential condition of their existence.

Metallic calcium may be obtained by decomposing fused calcium iodide with metallic sodium. It crystallises from the excess of sodium as the mass cools and may be isolated by dissolving the sodium in alcohol. It has a silvery appearance and is as hard as Iceland spar, very ductile and malleable. It melts at 760° C. and is lighter than barium and strontium, its sp. gr. being 1.56. It oxidises slowly in air at the ordinary temperature, but, when heated to redness, it fuses and burns with a very brilliant white light, being converted into lime (*calx*). It decomposes water at the ordinary temperature. Its salts impart a red colour to a colourless flame.

Carbonate of lime, or **Calcium carbonate** ($CaO.CO_2$ or $CaCO_3$), from which all the manufactured compounds of lime are derived, constitutes the different varieties of limestone which are met with in such abundance.

Chalk is simply calcium carbonate in an amorphous or uncrystallised state; it is known to the agriculturist as *mild lime*. Limestone consists of minute crystals of calc spar (see below). The *oolite* limestone, of which the Bath and Portland building-stones are composed, is so-called from its resemblance to the roe of fish (*ὠόν, an egg*). *Marble*, in its different varieties, is also an assemblage of minute crystals of calc spar, sometimes variegated by the presence of oxides of iron and manganese, or of bituminous matter. This last constituent gives the colour to black marble. Calcium carbonate is also found in large transparent rhombohedral crystals, which are known to mineralogists as *calcareous spar*, *calc spar*, or *Iceland spar*, and *calcite* (sp. gr. 2.7). When the crystals have the form of a six-sided prism, the mineral is termed *aragonite* (sp. gr. 2.94).

The attention of the crystallographer has long been directed to these two crystalline forms of calcium carbonate, on account of the circumstance that if a prism of aragonite be heated, it breaks up into a number of minute rhombohedra of calc spar. *Satin spar* is a variety of calcium carbonate. When slowly deposited from its solution in carbonic acid, calcium carbonate gives six-sided prisms of $CaCO_3.5Aq$. Precipitated calcium carbonate is amorphous, and is the least stable of the three forms and hence the most soluble (20 mgms. per litre). When heated to a high temperature it becomes aragonite, but when kept at moderate temperatures, in contact with the liquid from which it was precipitated, it becomes calcite.

Calcium carbonate is a chief constituent of the shells of fishes and of egg-shells, so that, except calcium phosphate, no mineral compound has so large a share in the composition of animal frames. *Corals* also consist chiefly of calcium carbonate

derived from the skeletons of innumerable minute insects. The mineral *gaylussite* is a double carbonate of calcium and sodium ($CaCO_3.Na_2CO_3.5Aq$), and is scarcely affected by water unless previously heated, when water dissolves out the sodium carbonate. *Baryta-calcite* is a double carbonate of barium and calcium ($BaCO_3.CaCO_3$).

The presence of calcium carbonate in spring waters and the solubility of this compound in a solution of carbon dioxide have already been considered (p. 56).

Lime (CaO).—The process by which lime is obtained from the carbonate has been already alluded to under the name of lime-burning. At a red heat calcium carbonate begins to decompose into CaO and CO_2; but unless the CO_2 be removed, it prevents further decomposition, so that marble or chalk cannot be completely decomposed in a covered crucible, and a lime-kiln must have a good draught to carry off the CO_2. At 812° C. the dissociation-pressure (p. 315) of $CaCO_3$ is 753 mm., and this is the best temperature for lime-burning.*

Accordingly, a kiln is commonly employed of the form of an inverted cone of brickwork (Fig. 213), and into this limestone and fuel are thrown in alternate layers. The former, losing its CO_2 before it reaches the

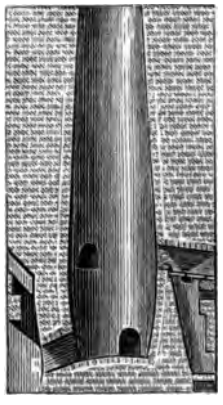


Fig. 213.—Limekiln.

Fig. 214.—Limekiln.

bottom of the furnace, is raked out in the form of *burnt* or *quick* lime (CaO), whilst its place is supplied by a fresh layer of limestone thrown in at the top of the kiln. Fig. 214 represents another form of kiln, in which the limestone is supported upon an arch built with large lumps of the stone above the fire, which is kept burning for about three days and nights, until the whole of the limestone is decomposed.

The usual test of the quality of the lime thus obtained consists in sprinkling it with water, with which it should eagerly combine, evolving much heat,† swelling to about $2\frac{1}{2}$ times its bulk, and crumbling to a light white powder of *calcium hydrate* (*slaked lime*), $Ca(OH)_2$. Lime which behaves in this manner is termed *fat lime;* whereas, if it be found to

* When precipitated $CaCO_3$ is heated to about 1000° C. under such conditions that none of its CO_2 can escape, it is converted into marble.

† The sudden slaking of a large quantity of lime may be a cause of fire. A rise of temperature to 150° C. frequently occurs. 56 grams of CaO evolve 15,540 gram units of heat when slaked.

slake feebly, it is pronounced a *poor lime*, and is known to contain a considerable proportion of foreign substances, such as silica, aluminia, magnesia, &c. Lime is said to be *overburnt* when it contains hard cinder-like masses of silicate of lime, formed by the combination of the silica, which is generally found in limestone, with a portion of the lime, under the influence of excessive heat in the kiln. *Air-slaked lime* has slaked by simple exposure to air; it has absorbed CO_2 as well as H_2O, and contains 57 per cent. $CaCO_3$ and 43 per cent. $Ca(OH)_2$.

Calcium hydroxide, $Ca(OH)_2$, is much less soluble in water than is barium or strontium hydroxide. It requires 700 parts of cold water to dissolve it, and twice as much hot water, so that *lime-water* always gives a precipitate when boiled. The solution is strongly alkaline, and readily absorbs CO_2 from the air, which precipitates $CaCO_3$. When lime water is evaporated *in vacuo* over H_2SO_4, it deposits small crystals of $Ca(OH)_2$.

$Ca(OH)_2$ is easily converted into CaO by heat. It is used in manufacturing chemistry as the cheapest alkaline substance.

197. Closely connected with limestone and lime is the **chemistry of building materials.**

Chemical principles would lead to the selection of pure silica (quartz, rock-crystal) as the most durable of building materials, since it is not attacked by any of the substances likely to be present in the atmosphere; but even if it could be obtained in sufficiently large masses for the purpose, its great hardness presents an obstacle to its being hewn into the required forms. Of the building stones actually employed, *granite*, *basalt*, and *porphyry* are the most lasting, on account of their capability of resisting for a great length of time the action of water and of atmospheric carbonic acid; but their hardness makes them so difficult to work, as to prevent their employment except for the construction of pavements, bridges, &c., where the work is massive and straightforward, and much resistance to wear and tear is required. The *millstone grit* is also a very durable stone, consisting chiefly of silica, and employed for the foundations of houses. *Freestone* is a term applied to any stone which is soft enough to be wrought with hammer and chisel, or cut with a saw; it includes the different varieties of sandstone and limestone. The *Yorkshire flags* employed for paving are siliceous stones of this description. The *Craigleith sandstone*, which is one of the freestones used in London, contains about 98 per cent. of silica, together with some calcium carbonate.

The building stones in most general use are the different varieties of calcium carbonate. The durability of these is in proportion to their compact structure; thus *marble*, being the most compact, has been found to resist for many centuries the action of the atmosphere, whilst the more porous limestones are corroded at the surface in a very short time. *Portland stone*, of which St. Paul's and Somerset House are built, and *Bath stone*, are among the most durable of these; but they are all slowly corroded by exposure to the atmosphere. The chief cause of this corrosion appears to be the mechanical disintegration caused by the expansion in freezing, of the water absorbed in the pores of the stone. In order to determine the relative extent to which different stones are liable to be disintegrated by frost, a piece of the stone may be saturated with water and alternately frozen and thawed. *Magnesian limestones*

(carbonate of calcium with carbonate of magnesium) are much valued for ornamental architecture, on account of the ease with which they may be carved, and are said to be more durable in proportion as they approach the composition expressed by the formula $CaCO_3.MgCO_3$.* The magnesian limestone from Bolsover Moor, of which the Houses of Parliament are built, contains 50 per cent. of calcium carbonate, 40 of magnesium carbonate, with some silica and alumina.

It is probable that a slow corrosion of the surface of limestone is effected by the carbonic acid continually deposited in aqueous solution from the air; and it is certain that in the atmosphere of towns the limestone is attacked by the sulphuric acid which results from the combustion of coal and the operations of chemical works. The Houses of Parliament have suffered severely, probably from this cause. Many processes have been recommended for the preservation of building stones, such as waterproofing them by the application of oily and resinous substances, and coating or impregnating them with solution of soluble glass and similar matters; but none seems yet to have been thoroughly tested by practical experience.

Purbeck, *Ancaster*, and *Caen stones* are well-known limestones employed for building.

The *mortar* employed for building is composed of 1 part of freshly slaked lime and 2 or 3 parts of sand intimately mixed with enough water to form a uniform paste. The hardening of such a composition appears to be due, in the first instance, to the absorption of carbon dioxide from the air, by which a portion of the lime is converted into calcium carbonate, and this, uniting with the unaltered calcium hydrate, forms a solid layer, adhering closely to the two surfaces of brick or stone, which it cements together. In the course of time the lime would act upon the silica, producing calcium silicate, and this chemical action would render the adhesion more perfect. The chief use of the sand here, as in the manufacture of pottery (*q.v.*) is to prevent excessive shrinking during the drying of the mortar.

In constructions which are exposed to the action of water, mortars of peculiar composition are employed. These *hydraulic mortars*, or *cements*, as they are termed, are prepared by calcining mixtures of calcium carbonate with from 10 to 30 per cent. of clay, when carbonic acid gas is expelled, and the lime combines with a portion of the silica and alumina from the clay, producing tricalcium silicate, $3CaO.SiO_2$, and tricalcium aluminate, $3CaO.Al_2O_3$. When the calcined mass is ground to powder and mixed with water these silicates combine with water to form hydrated silicates (with liberation of free lime), which dissolve in the water and immediately crystallise again (in the manner described for the setting of plaster of Paris), thus causing the cement to set. *Roman cement* is prepared by calcining a limestone containing about 25 per cent. of clay, and hardens in a very short time after mixing with water. For *Portland cement* (so-called from its resembling Portland stone) a mixture of river-mud (chiefly clay) and limestone is calcined at a very high temperature.

Hydraulic cements are mixed for use with sand before they are wetted with water. *Concrete* is a mixture of hydraulic cement (1 vol.)

* Any excess of calcium carbonate above that required by this formula may be dissolved out by treating the powdered magnesium limestone with weak acetic acid.

with sand (2 vols.) and small gravel (4 vols.), the last being known as the "aggregate."

Scott's cement is a mixture of quick-lime with a small proportion of calcium sulphate.

Calcium dioxide, CaO_2, is precipitated in combination with $8H_2O$, when solution of sodium peroxide is added to one of a calcium salt.

Calcium nitrate, $Ca(NO_3)_2.4Aq$, differs from those of Ba and Sr by being deliquescent, much more soluble in water, and soluble in alcohol. It occurs in well-waters and in soils, the NO_3 having been formed by oxidation of NH_3.

198. **Sulphate of lime, or Calcium sulphate,** in combination with water ($CaSO_4.2H_2O$), is met with in nature, both in the form of transparent prisms of *selenite*, and in opaque and semi-opaque masses known as *alabaster* and *gypsum*. It is this latter form which yields *plaster of Paris*, for when heated to between 150° and 200°C. it loses $\frac{3}{4}$ of its water, becoming $2CaSO_4.H_2O$, and if the mass be then powdered, and mixed with water, the powder recombines with the water to form a mass, the hardness of which nearly equals that of the original gypsum.

In the preparation of plaster of Paris, a number of large lumps of gypsum are built up into a series of arches, upon which the rest of the gypsum is supported; under these arches the fuel is burnt, and its flame is allowed to traverse the gypsum, care being taken that the temperature does not rise too high, lest the gypsum be *overburnt* and set very slowly with water. When the operation is supposed to be completed, the lumps are carefully sorted, and those which appear to have been properly calcined are ground to a very fine powder. When this powder is mixed with water to a cream, and poured into a mould, the minute particles of calcium sulphate combine with water to reproduce the original gypsum ($CaSO_4.2H_2O$), and this act of combination is attended with a slight expansion which forces the plaster into the finest lines of the mould.

The setting is due to the fact that a small portion of the plaster ($2CaSO_4.H_2O$) dissolves in the water, crystallising again immediately as $CaSO_4.2H_2O$, thus leaving the water free to dissolve another portion of $2CaSO_4.H_2O$, which crystallises in its turn as $CaSO_4.2H_2O$. Thus the mass soon becomes one of interlaced crystals of $CaSO_4.2H_2O$. An addition of one-tenth of lime to the plaster hardens it and accelerates the setting.

It is not known why overburnt gypsum does not set, or sets only very slowly, but it is supposed to be due to the fact that there is no nucleus of undecomposed gypsum in it. This view is supported by the behaviour of anhydrous Na_2SO_4, which remains as a powder under water until a crystal of the hydrated salt is added, when the whole mass solidifies.

The transition-point from $CaSO_4.2H_2O$ to $2CaSO_4.H_2O$ is 107° C., at which temperature the pressure of the water vapour from the gypsum is higher than that of the vapour from water itself at this temperature. It follows that when gypsum is heated in a sealed tube the water vapour condenses, and the gypsum becomes a magma of plaster of Paris in water. The change at 107° C. is exceedingly slow, so that the gypsum-burner is obliged to use a considerably higher temperature than this.

Stucco consists of plaster of Paris (occasionally coloured) mixed with a solution of size; certain cements used for building purposes are prepared from burnt gypsum, which has been soaked in a solution of alum and again burnt; and although the plaster thus obtained takes much longer to set than the ordinary kind, it is much harder, and therefore takes a good polish. A similar hardening of objects cast from plaster of Paris is effected by soaking them in solution of $KHSO_3$, probably owing

to the slow formation of a double salt of $CaSO_4$ and K_2SO_4: this is applied in the making of artificial marble. Plaster of Paris is much damaged by long exposure to moist air, from which it regains a portion of its water, and its property of setting is so far diminished. Precipitated calcium sulphate is used by paper-makers under the name of *pearl hardener*. Calcium sulphate is useful in the farmyard and stables for absorbing the ammonia of the decomposing excrements, which would otherwise be lost to the manure.

$CaSO_4$ forms the mineral *anhydrite*, a bed of which, when exposed to the air in a railway cutting, has been known to increase in bulk by absorbing water to such an extent as to disturb the stability of the sides of the cutting. Calcium sulphate is contained in most natural waters, and is one of the chief causes of the *permanent hardness* which is not removed by boiling. It is much more soluble in water than is strontium sulphate, so that sulphates will precipitate calcium only from strong solutions. The aqueous solution of $CaSO_4$ precipitates barium salts immediately, but strontium salts only after an interval, on account of the greater solubility of $SrSO_4$. The calcium sulphate is more soluble in water at 35° C. than at any other temperature, 1 part of $CaSO_4$ then dissolving in about 400 parts of water. It is insoluble in alcohol. Boiling HCl dissolves it, and deposits it in needles on cooling.

Calcium chloride ($CaCl_2$) has been mentioned as the residue left in the preparation of ammonia. The pure salt may be obtained by dissolving pure calcium carbonate (*Iceland spar*) in hydrochloric acid, and evaporating the solution, when prismatic crystals of the composition $CaCl_2.6Aq$ are obtained, which dissolve in one-fourth of their weight of cold water. When these are heated they melt at 29° C., and at about 200° C. are converted into a white porous mass of $CaCl_2.2Aq$, which is much used for drying gases. At a higher temperature, fused calcium chloride, free from water, is left; this is very useful for removing water from some liquids. When heated in air, it evolves chlorine and becomes alkaline. A saturated (325 per cent.) solution of calcium chloride boils at 355° F. (180° C.), and is sometimes used as a convenient bath for obtaining a temperature above the boiling-point of water. When mixed with snow the crystals $CaCl_2.6H_2O$ form a cryohydrate, reducing the temperature to −48° C. In consequence of the attraction of calcium chloride for water, surfaces wetted with a solution of the salt never get dry. Rope mantlets, for the protection of gunners, are saturated with it to prevent their taking fire. Calcium chloride is easily soluble in alcohol.

When $Ca(OH)_2$ is boiled with a strong solution of calcium chloride, it is dissolved, and the filtered solution deposits prismatic crystals of *calcium oxychloride*, $CaCl_2.3CaO.15Aq$, which are decomposed by water.

Chloride of lime; see p. 183.

Calcium fluoride, CaF_2, already described as *fluor spar* (p. 202), occurs in the bones and teeth. Many specimens of it decrepitate and emit a phosphorescent light when heated. It fuses at a red heat, and is used in metallurgy as a flux, since it attacks silicates at a high temperature. Calcium fluoride is slightly soluble in hot HCl, and is reprecipitated by NH_3. It is obtained as a gelatinous precipitate insoluble in acetic acid when $CaCl_2$ is added to an alkali fluoride. Artificial teeth are made of calcium fluoride.

Calcium sulphide (CaS) is present in *Balmain's luminous paint*. Its property of shining in the dark after exposure to a bright light was observed by Canton in 1761;

his so-called *phosphorus* was obtained by strongly heating oyster-shells with sulphur. The phosphorescence is not due to slow oxidation, since a specimen which has been kept for more than a century in a sealed tube still exhibits it; it does not appear to be a property of the pure sulphide.

When CaO is acted on by H_2S it yields a crystalline *calcium hydrosulphide*, $Ca(SH)_2$. When this is heated in H_2S it is decomposed; $Ca(SH)_2 = CaS + H_2S$. The CaS is a white solid, soluble in water. When $Ca(SH)_2$ is exposed to air it deliquesces, evolves H_2S, and becomes Ca(SH)(OH); $Ca(SH)_2 + H_2O = H_2S + Ca(SH)(OH)$. Calcium sulphide occurs, combined with CaO, in the *tank-waste* of the alkali works. A solution of $Ca(SH)_2$ is used as a depilatory.

Calcium phosphate, $Ca_3(PO_4)_2$, occurs in the minerals *apatite*, *phosphorite*, *sombrerite*, and *coprolite*; in the two first it is combined with calcium fluoride, forming $3Ca_3(PO_4)_2.CaF_2$, and this is also contained in bone ash, of which $Ca_3(PO_4)_2$ forms the larger proportion (80 per cent.). This is sold as a *non-mercurial plate powder*, under the name of *white rouge*. Calcium phosphate is nearly insoluble in water, but it is dissolved by HCl or HNO_3, and is precipitated again by ammonia. When $CaCl_2$ is added to Na_2HPO_4, a gelatinous precipitate is obtained, which becomes crystalline after a short time. The gelatinous precipitate dissolves easily in acetic acid, but the crystalline precipitate does not, and if the solution of the gelatinous precipitate in very little acetic acid be allowed to stand, or briskly stirred, it deposits crystals of $CaHPO_4.2Aq$. This salt is found in calculi in the sturgeon.

Tetra-hydrogen calcium phosphate, $CaH_4(PO_4)_2$, commonly called **superphosphate of lime,** is made by decomposing $Ca_3(PO_4)_2$ with sulphuric acid; $Ca_3(PO_4)_2 + 2H_2SO_4 = CaH_4(PO_4)_2 + 2CaSO_4$; the calcium sulphate is filtered off, and the superphosphate is left in solution. The pure superphosphate may be prepared by dissolving bone-ash in HCl, precipitating with ammonia, and digesting the washed precipitate of $Ca_3(PO_4)_2$ with H_3PO_4; $Ca_3(PO_4)_2 + 4H_3PO_4 = 3CaH_4(PO_4)_2$. On allowing the solution to evaporate spontaneously, the salt crystallises in rhomboidal plates containing a molecule of water. It is dissolved by a small quantity of water, but it is decomposed and precipitated by much water, or by boiling; $CaH_4(PO_4)_2 = H_3PO_4 + CaHPO_4$.

The commercial superphosphate manure is a damp mixture of $CaH_4(PO_4)_2$ and $CaSO_4$, prepared by mixing ground mineral phosphates with sulphuric acid. It is valued by the agriculturist for the large amount of soluble phosphate which it contains; in course of time, the proportion of this decreases, and the phosphate is said to have *reverted* to the insoluble form, owing to the action of the superphosphate upon some undecomposed $Ca_3(PO_4)_2$ remaining in the compound, resulting in the formation of the insoluble hydrocalcium phosphate—$CaH_4(PO_4)_2 + Ca_3(PO_4)_2 = 4CaHPO_4$. Another cause for this *retrogression* of the superphosphate which has been prepared from mineral phosphates, is the presence of the sulphates of aluminium, magnesium, and iron, which gradually convert the phosphoric acid into insoluble forms.

Calcium pyrophosphate, $Ca_2P_2O_7$, when exposed for several hours to a dull red heat, forms a perfectly transparent glass of sp. gr. 2.6, which may be worked into prisms and lenses like ordinary glass, its refractive power being equal to that of crown glass. It is not acted on by acids in the cold, and even resists HF.

Calcium ammonium arsenate, $CaNH_4AsO_4.7Aq$, is obtained as a white precipitate by mixing $CaCl_2$ with excess of NH_3, and adding arsenic acid. The precipitate is gelatinous at first, but changes rapidly into fine needles, especially if stirred. It is slightly soluble in water, but almost insoluble in ammonia. Dried *in vacuo*, over sulphuric acid, it becomes $Ca_3NH_4H_3(AsO_4)_3.3Aq$. Dried at 100° C., it has the formula $Ca_3NH_4H_3(AsO_4)_3.3Aq$. Heated to redness, it becomes *calcium pyro-arsenate*, $Ca_2As_2O_7$. *Calcium ortho-arsenate*, $Ca_3(AsO_4)_2$, and *metarsenate*, $Ca(AsO_3)_2$, have also been obtained.

Calcium carbide, CaC_2. Some of the properties of this substance have been described at p. 137. Its manufacture is conducted by feeding a mixture of 100 parts of powdered quicklime with 80 parts of powdered coke between the poles of an electric arc, when the materials fuse, having reacted to form calcium carbide; $CaO + C_3 = CaC_2 + CO$. Several forms of electric furnace have been devised for this manufacture; one of them consists of an iron truck contained in a brickwork chamber, and having suspended in it a bundle of carbon rods. The latter are connected with one pole of the dynamo, the truck being connected with the other pole, and thus conducting the current to the charge it contains, which forms the actual electrode and protects the truck from the heat. The truck is run out of the furnace and another substituted for it as soon as it is full of the carbide.

Pure calcium carbide forms colourless transparent crystals, but the commercial product is a grey opaque crystalline substance of sp. gr. 2.2, which is decomposed by aqueous vapour so that it smells of impure acetylene when exposed to the atmosphere (p. 137).

Calcium silicates are found associated with other silicates in many materials. They are also constituents of most forms of glass, which will therefore receive attention here.

199. **Glass** is defined chemically to be an amorphous mixture of two or more silicates, one of which is a silicate of an alkali-metal, the other being a silicate of calcium, barium, iron, lead, or zinc. Typical glass may be said to correspond with the formula $M_2CaSi_6O_{14}$, where M is an alkali metal. The different kinds of glass may, however, vary considerably from this formula.

If silica be fused with an equal weight of carbonate of potassium or sodium, a transparent glassy mass is obtained, but this is slowly dissolved by water, and would therefore be incapable of resisting the action of the weather; if a small proportion of lime or baryta, or of the oxides of iron, lead, or zinc, be added, the glass becomes far less easily affected by atmospheric influences.

The most valuable property of glass, after its transparency and permanence, is that of assuming a viscid or plastic consistence when fused, which allows it to be so easily fashioned into the various shapes required for use or ornament.

The composition of glass is varied according to the particular purpose for which it is intended, the materials selected being fused in large clay crucibles placed in reverberatory furnaces, and heated by a coal fire or in a gas-furnace.

Ordinary *window glass* is a *soda* glass, essentially composed of sodium silicate and calcium silicate, containing one molecule (13.3 %) of soda, one molecule (12.9 %) of lime, and five molecules (69.1 %) of silica; it also usually contains a little alumina. This variety of glass is manufactured by fusing sand (100 parts) with chalk (35) and soda-ash (35): a considerable quantity of broken window glass is always fused up at the same time. Of course, CO_2 is expelled from the chalk and the Na_2CO_3 in the gaseous state; and in order that this may not cause the contents of the crucible to froth over during the fusion, the materials are first *fritted* together, as it is termed, at a temperature insufficient to liquefy them, when the CO_2 is evolved gradually, and the fusion afterwards occurs without effervescence.

Occasionally, sodium sulphate is employed instead of the carbonate, when it is usual to add a small proportion of charcoal in order to facilitate the decomposition of the sulphate by removing part of its oxygen ($Na_2SO_4 + SiO_2 + C = Na_2SiO_3 + SO_2 + CO$). Before the glass is worked into sheets, it is allowed to remain at rest for some time in the fused state, so that the air-bubbles may escape, and the *glass-gall* or scum

(consisting chiefly of sodium sulphate and sodium chloride), which rises to the surface, is removed.

Plate glass is also chiefly a silicate of sodium and calcium, but it contains, in addition, a considerable quantity of silicate of potassium (74 per cent. of SiO_2, 12 of Na_2O, 5.5 of K_2O, and 5.5 of CaO). The purest white sand is selected, and great care is taken to exclude impurities.

Crown glass, used for optical purposes, contains no sodium, since that metal has the property of imparting a greenish tint to glass, which is not the case with potassium. This variety of glass, therefore, is prepared by fusing sand with potassium carbonate and chalk in such proportions that the glass may contain 1 mol. (22 %) of K_2O, 1 mol. (12.5 %) of CaO, and 4 mols. (62 %) of SiO_2.

Bohemian glass, also a *potash* glass (silicate of K_2O and CaO), is less fusible than soda glass, and less easily attacked by acids; hence its use for chemical vessels; it appears to owe its infusibility to its high content of silica.

The alkali silicate in glass being the more soluble in water the richer it is in alkali, a glass containing a high percentage of silica is the more generally useful for chemical vessels, particularly as it is less fusible than that poorer in this constituent. It is only comparatively recently, however, that furnaces attaining the high temperatures necessary for working glass rich in silica have been used. As stated at p. 279 the introduction of the electric furnace may enable pure silica to be substituted for glass.

Acid solutions attack glass less than water does, while alkali produces the most effect. By steaming the glass for some time its surface becomes more resistant. Glass containing both alkalies is more easily attacked than that containing only one.

The glass of which *wine bottles* are made is of much cheaper and commoner description, consisting chiefly of calcium silicate, but containing, in addition, small quantities of the silicates of sodium, of aluminium, and of iron, to the last of which it owes its dark colour.

Flint glass, which is used for table glass and for ornamental purposes, is a double silicate of potassium and lead, containing one mol. (13.67 %) of K_2O, one mol. (33.28 %) of PbO, and six mols. (51.93 %) of SiO_2. It is prepared by fusing 300 parts of the purest white sand with 200 parts of minium (red oxide of lead), 100 parts of refined pearl-ash, and 30 parts of nitre. The fusion is effected in crucibles covered in at the top to prevent the access of the flame, which would reduce a portion of the lead to the metallic state. The nitre is added in order to oxidise any accidental impurities which might reduce the lead.

The presence of the lead in glass very much increases its fusibility, and renders it much softer, so that it may be more easily cut into ornamental forms; it also greatly increases its lustre and beauty.

Barium has also the effect of increasing the fusibility of glass, and zinc, like lead, increases its brilliancy and refracting power, on which account it is employed in some kinds of glass for optical purposes. Glass of this description is also made by substituting boric oxide for a portion of the silica.

All glass articles must be *annealed* by being slowly cooled, otherwise they are liable to spontaneous fracture, due to the excessive strains produced in the structure of the glass.

Some varieties of glass, if heated nearly to their melting-point, and allowed to cool slowly, become converted into an opaque very hard mass resembling porcelain (*Réaumur's porcelain*). This change, which is known as *devitrification*, is due to the crystallisation of the silicates contained in the mass, and, by again fusing it, the glass may be restored to its original transparent condition.

Toughened glass is made by heating the glass vessel to its softening point, immersing it in a bath of oil or steam at 200° C., and cooling it quickly. This treatment hardens it, increases its specific gravity, and renders it less brittle externally, but puts the inner portion in a state of tension, so that it sometimes breaks up spontaneously.

In producing *coloured glass*, advantage is taken of its property of dissolving many metallic oxides with production of peculiar colours. It has been mentioned above that bottle glass owes its green colour to the presence of iron; and since this metal is generally found in small quantity in sand, and even in chalk, it occasionally happens that a glass which is required to be perfectly colourless turns out to have a slight green tinge.

In order to remove this, a small quantity of some oxidising agent is usually added, in order to convert the ferrous oxide into ferric oxide, which does not impart any colour when present in minute proportion. A little nitre is sometimes added for this purpose, or some white arsenic, which yields its oxygen to the ferrous oxide, and escapes in the form of vapour of arsenic; red oxide of lead (Pb_3O_4) may also be employed, and is reduced to oxide of lead (PbO), which remains in the glass. Manganese dioxide (*glassmaker's soap*) is often added as an oxidising agent, being reduced to the state of manganous oxide (MnO), which does not colour the glass; but care is then taken not to add too much of the dioxide, for a very minute quantity of this substance imparts a beautiful amethyst-purple colour to glass.

Suboxide of copper is used to produce a red glass, and the finest ruby glass is obtained by the addition of a little gold. The oxides of antimony impart a yellow colour to glass; a peculiar brown-yellow shade is given by charcoal in a fine state of division, and sesquioxide of uranium produces a fine greenish-yellow glass. Green glass is coloured either by oxide of copper or sesquioxide of chromium, whilst oxide of cobalt gives a magnificent blue colour. For black glass a mixture of the oxides of cobalt and manganese is employed. The white enamel glass is a flint glass, containing about 10 per cent. of binoxide of tin. Bone-ash is also used to impart this appearance to glass. The *irisation* of glass, giving it the tints of mother-of-pearl, is effected by corroding its surface with hydrochloric acid of 15 per cent. strength, under heat and pressure.

Kryolite is employed in making *opal-glass* containing 64 per cent. of silica, 17 of alumina, 16 of lead oxide, and 3 of potash.

200. **General review of the metals of the alkaline earths.**—Barium, strontium, and calcium form a highly interesting natural group of metals related to each other in a most remarkable manner. They exhibit a marked gradation in their attraction for oxygen: barium is more readily tarnished or oxidised, even in dry air, than strontium, and strontium more readily than calcium. The hydroxides of the metals exhibit a similar gradation in properties; barium hydroxide does not lose water, however strongly it may be heated, whereas the hydroxides of strontium and calcium are decomposed at a red heat. Then barium hydroxide and strontium hydroxide are far more soluble in water than is calcium hydroxide, and all these three exhibit a very decided alkaline reaction which entitles them to the name of *alkaline earths*.

Among the other compounds of these metals, the sulphates may be named as presenting a gradation of a similar description; for barium sulphate may be said to be insoluble in water, strontium sulphate

dissolves to a very slight extent, and calcium sulphate is much more soluble.

The manner in which these metals are associated in nature is also not without its significance: for if two of them are found in the same mineral they will usually be those which stand next to each other in the group; thus strontium carbonate is found together with barium carbonate in witherite, whilst calcium carbonate is associated with strontium sulphate in celestine. Again, strontium carbonate is often found with calcium carbonate in aragonite. Such facts lend support to the hypotheses of Crookes and others as to the possible *evolution* of the elements.

MAGNESIUM.

$Mg'' = 24.2$ parts by weight.

201. Magnesium is found, like calcium, though less abundantly, in each of the three natural kingdoms. Among minerals containing this metal, those with which we are most familiar are certain combinations of silica and magnesia (silicates of magnesium) known by the names of *talc*, *steatite* or *French chalk*, *asbestos*, and *meerschaum*, which always contains water. *Magnesite* is a carbonate of magnesium. Most of the minerals containing magnesium have a remarkably soapy feel. The compounds of magnesium, which are employed in medicine, are derived either from the mineral *dolomite*, or *magnesian limestone*, which contains the carbonates of magnesium and calcium, or from the magnesium sulphate which is obtained from sea water and from the waters of many mineral springs.

Metallic magnesium is important as a source of light. When the extremity of a wire of this metal is heated in a flame, it takes fire, and burns with a dazzling white light,* becoming magnesia (MgO). If the burning wire be plunged into a bottle of oxygen, the combustion is still more brilliant. The light emitted by burning magnesium induces chemical changes similar to those caused by sunlight, a circumstance turned to advantage for the production of photographic pictures, for which purpose the powdered metal is blown through a flame producing a flash of very short duration but intense luminosity. Attempts have been made to introduce magnesium as an illuminating agent for general purposes, but the large quantity of solid magnesia produced in its combustion forms a very serious obstacle to its use. The metal is obtained by electrolysing fused *carnallite* (p. 335), which, when melted, loses its water and becomes $KCl.MgCl_2$. The liquid is contained in an iron vessel externally heated and serving as the cathode. The anode is a carbon rod surrounded by a porous cylinder and partly immersed in the fused mass. The metal separates at the cathode and floats on the top of the liquid, while the chlorine escapes at the anode and is kept from the metal by the porous cylinder. To prevent the Mg from burning the atmosphere in the vessel must be nitrogen. This electrolysis has displaced the older method of reducing $MgCl_2$ by fusing it with sodium.

* A wire of 0.33 millimetre diameter gives a light of 74 candle-power. Although the illuminating power of the sun's rays is 524 times that of burning Mg, their chemical activity is only 5 times as great. The heat of combustion is $Mg,O = 143{,}400$ calories.

In most of its physical and chemical characters, magnesium resembles zinc, though its colour more nearly approaches that of silver; in ductility and malleability, it also surpasses zinc. It is nearly as light, however, as calcium, its specific gravity being 1.74. It fuses about 750° C., and may be distilled like zinc. Cold water has scarcely any action upon magnesium; even when boiled, it oxidises the metal very slowly. In the presence of acids, however, it is rapidly oxidised by water. Solution of ammonium chloride also dissolves it, owing to the tendency of the magnesium salts to form double salts with those of ammonium; $4NH_4Cl + Mg = (NH_4)_2MgCl_4 + H_2 + 2NH_3$. Magnesium is one of the few elements which unite directly with nitrogen at a high temperature. The *magnesium nitride*, Mg_3N_2, has been obtained in transparent crystals, and is evidently composed after the type $2NH_3$, so that it is not surprising that the action of water upon it gives rise to magnesia and ammonia; $Mg_3N_2 + 3H_2O = 2NH_3 + 3MgO$. If a foot of Mg tape be burnt in air, the residue evolves much NH_3 when boiled with water.

Magnesia, MgO, occurs, crystallised in octahedra, as the mineral *periclase*. It is prepared by decomposing magnesium carbonate by heat, and is a light white powder, very infusible (so that it is used for making basic fire-bricks) and scarcely affected by water. It dissolves easily in acids. *Magnesium hydroxide*, $Mg(OH)_2$, also occurs crystallised as *brucite*. When MgO is mixed with water, combination occurs, but not with much evolution of heat, as with BaO, SrO, and CaO. If excess of water be avoided, the mass *sets* like plaster of Paris. $Mg(OH)_2$ is precipitated when an alkali is added to a magnesium salt. The hydroxide slowly absorbs CO_2 from the air, and is easily decomposed by heat into MgO and H_2O. It is used in extracting sugar from the beet.

Magnesium carbonate, $MgCO_3$, is found as *magnesite*, which is imported from Greece. It is unaffected by water, and does not effervesce so briskly with acids as do the other carbonates. It is easily decomposed by heat into MgO and CO_2. When a salt of magnesium is precipitated by an alkali carbonate, the precipitate is not the normal carbonate, as in the cases of Ba, Sr, and Ca, but a basic carbonate, or a compound of the carbonate and hydroxide. Ordinary *magnesia alba*, or *light* carbonate of magnesia, is prepared by precipitating magnesium sulphate with sodium carbonate, and boiling; it generally has the composition $5MgCO_3.2Mg(OH)_2.7Aq$. In preparing the *heavy* carbonate, the mixed solutions are evaporated to dryness, and the sodium sulphate washed out of the residue by water. These light and heavy carbonates, when calcined, yield light and heavy magnesia, the former having $3\frac{1}{2}$ times the bulk of the latter.

Magnesium carbonate, like $CaCO_3$, is soluble in carbonic acid, and is present in most natural waters, causing temporary hardness, the $MgCO_3$ being precipitated by boiling. When magnesia alba is dissolved in carbonic acid water, and the solution exposed to air, needles of $MgCO_3.3Aq$ are deposited. If this be boiled with water, it loses CO_2, and becomes a basic carbonate.

Dolomite or *magnesium limestone*, is a mixture of magnesium carbonate and calcium carbonate in variable proportions. Magnesium carbonate is prepared from it by heating it sufficiently to decompose the $MgCO_3$, and exposing it, under pressure, to the action of water and CO_2, when the MgO is dissolved and the $CaCO_3$ is left. By passing steam through

the solution, the basic magnesium carbonate is precipitated. *Pearl spar* is a crystalline form of the double carbonate, $MgCa(CO_3)_2$.

The sulphate of magnesia or magnesium sulphate, so well known as Epsom salts, is sometimes prepared by calcining dolomite to expel the CO_2, washing the residual mixture of lime and magnesia with water to remove part of the lime, and treating it with sulphuric acid, which converts the calcium and magnesium into sulphates; and since calcium sulphate is almost insoluble in water, it is readily separated from the magnesium sulphate which passes into the solution, and is obtained by evaporation in prismatic crystals, having the composition $MgSO_4.H_2O.6Aq$. Epsom salts are now made from *Kieserite*, $MgSO_4.H_2O$, found in the Stassfurt salt beds. This is almost insoluble in water, but, when kept in contact with it, is slowly converted into $MgSO_4.7H_2O$. The preparation of Epsom salts from sea water has already been alluded to (p. 344).

In some parts of Spain, magnesium sulphate is found in large quantities (like nitre in hot climates) as an efflorescence upon the surface of the soil. This sulphate, as well as that contained in well-waters, appears to have been produced by the action of the calcium sulphate, originally present in the water, upon magnesian limestone rocks: $MgCO_3 + CaSO_4 = MgSO_4 + CaCO_3$.

The crystals $MgSO_4.7H_2O$ fuse easily, and become $MgSO_4.H_2O$ at 150° C. The last H_2O, can only be expelled at above 200°, and is termed the *water of constitution.*

The water of constitution in the magnesium sulphate may be displaced by the sulphate of an alkali-metal without alteration in its crystalline form; a double sulphate of magnesium and potassium ($MgSO_4.K_2SO_4.6Aq$), and a similar salt of ammonium may be thus obtained. The mineral *polyhalite* (πολύς, *many*, ἅλς, *salt*) is a remarkable salt, containing $MgSO_4.K_2SO_4.2CaSO_4.2H_2O$.* Water decomposes it into its constituent salts.

Epsom salts dissolve very easily in water, but not in alcohol. If the aqueous solution be mixed with enough alcohol to render it turbid, small oily drops separate, from which small crystals presently shoot out, and the liquid becomes, by degrees, a pasty mass of very light needles closely interlaced. These contain $7H_2O$. An aqueous solution crystallised at above 70° C. deposits $MgSO_4.H_2O.5Aq$; at 0°, crystals of $MgSO_4.H_2O.11Aq$ are formed.

Phosphates of magnesium.—$Mg_3(PO_4)_2$ is contained in bones and in some seeds. $MgHPO_4.7Aq$ is the precipitate produced by Na_2HPO_4 in magnesium salts; it is decomposed by boiling with water; $3MgHPO_4 = H_3PO_4 + Mg_3(PO_4)_2$. $MgNH_4PO_4.6Aq$ is deposited in crystals from alkaline urine, and forms *triple phosphate* calculi. It is precipitated by Na_2HPO_4 from a magnesium salt to which NH_3 has been added; $MgSO_4 + NH_3 + Na_2HPO_4 = Na_2SO_4 + MgNH_4PO_4$. Ammonium chloride should be added first to prevent the separation of $Mg(OH)_2$. The precipitation is much promoted by stirring; the $MgNH_4PO_4$ is sparingly soluble in water, and almost insoluble in ammonia; when it is heated to redness, $2MgNH_4PO_4 = Mg_2P_2O_7 + NH_3 + H_2O$. In quantitative analysis, Mg and P are generally determined in this form.

Magnesium-ammonium arsenate, $MgNH_4AsO_4.6H_2O$, is very similar, and is used in determining arsenic.

Magnesium borate and chloride compose the mineral *stassfurtite; hydroboracite* is a hydrated borate of calcium and magnesium.

Serpentine, $2SiO_2.3(Mg,Fe)O$, and *olivine*, $SiO_2.3(Mg,Fe)O$, are silicates of magnesia and ferrous oxide. Some of the varieties of serpentine are used for preparing the compounds of magnesium, being easily decomposed by acids with separation of silica. The minerals, *asbestos*, *meerschaum*, *steatite*, and *talc* consist chiefly of magnesium silicates.

Magnesium chloride occurs in sea-water, in brine-springs, in many natural waters and in the minerals *carnallite* (p. 335) and *bischofite*,

* Polyhalite is found in the salt-beds of Stassfurt. *Kainite*, from the same locality, is $K_2SO_4.MgSO_4.MgCl_2.6Aq$.

$MgCl_2.6Aq$. It is easily obtained in solution by neutralising hydrochloric acid with magnesia or its carbonate; but if this solution be evaporated in order to obtain the dry chloride, a considerable quantity of the salt is decomposed by the water at the close of the evaporation, leaving much magnesia mixed with the chloride ($MgCl_2 + H_2O = 2HCl + MgO$). This decomposition may be prevented by mixing the solution with three parts of chloride of ammonium for every part of magnesia, when a double salt, $MgCl_2.2NH_4Cl$, is formed, which may be evaporated to dryness without decomposition, and leaves fused magnesium chloride when further heated, the ammonium chloride being volatilised. The magnesium chloride absorbs moisture very rapidly from the air, and is very soluble in water. Like all the soluble salts of magnesium, it has a decidedly bitter taste. When magnesia is moistened with a strong solution of magnesium chloride, it sets into a hard mass like plaster of Paris, apparently from the formation of an oxychloride. It may be mixed with several times its weight of sand, and will bind the sand firmly together.

The *ammonium magnesium* chloride, $NH_4Cl.MgCl_2.Aq$, is not decomposed by ammonia, which therefore gives no precipitate in solutions of magnesium to which NH_4Cl has been added in sufficient quantity.

Magnesium stands apart from other metals, on the one hand, by the non-precipitation of its sulphide, and, on the other, by the tendency of all its salts, except the phosphate and arsenate, to form soluble compounds with the salts of ammonium.

ZINC.

Zn″ = 65 parts by weight = 2 vols.

202. Zinc occupies a high position among useful metals, being peculiarly fitted, on account of its lightness, for the construction of gutters, water-pipes, and roofs of buildings, and possessing for these purposes a great advantage over lead, since the specific gravity of the latter metal is about 11.5, whilst that of zinc is only 7. For such applications as these, where great strength is not required, zinc is preferable to iron, on account of its superior malleability; for although a bar of zinc breaks under the hammer at the ordinary temperature, it becomes so malleable at 250° F. (121° C.) as to admit of being rolled into thin sheets. This malleability of zinc when heated was discovered only in the commencement of the last century, until which time the sole use of the metal was in the manufacture of brass. When zinc is heated to 400° F. (204° C.), it again becomes brittle, and may be powdered in a mortar. The easy fusibility of zinc also gives it a great advantage over iron, as rendering it easy to be cast into any desired form; indeed, zinc is surpassed in fusibility (among the metals in ordinary use) only by tin and lead, its melting-point being below a red heat, and usually estimated at 786° F. (410° C.). Zinc is also less liable than iron to corrosion under the influence of moist air, for although a bright surface of zinc soon tarnishes when exposed to the air, it merely becomes covered with a thin film of zinc oxide (passing gradually into basic carbonate, by absorption of CO_2 from the air) which protects the metal from further action.

The great strength of iron has been ingeniously combined with the durability of zinc, in the so-called *galvanised iron*, which is made by

coating clean iron with melted zinc, thus affording a protection much needed in and around large towns, where the sulphurous and sulphuric acids arising from the combustion of coal, and the acid emanations from various factories, greatly accelerate the corrosion of unprotected iron. The iron plates to be coated are first thoroughly cleansed by a process which will be more particularly noticed in the manufacture of tin-plate, and are then dipped into a vessel of melted zinc, the surface of which is coated with sal ammoniac (ammonium chloride) in order to dissolve the zinc oxide which forms upon the surface of the metal, and might adhere to the iron plate so as to prevent its becoming uniformly coated with the zinc.* A more firmly adherent coating of zinc is obtained by first depositing a thin film of tin upon the surface of the iron plate by galvanic action, and hence the name *galvanised* iron.

The ores of zinc are found pretty abundantly in England, chiefly in the Mendip Hills in Somersetshire, at Alston Moor in Cumberland, in Cornwall and Derbyshire, but the greater part of the zinc used in this country is imported from Belgium and Germany, being derived from the ores of Transylvania, Hungary, and Silesia.

Metallic zinc is never met with in nature. Its chief ores are *calamine* or zinc carbonate ($ZnCO_3$), *blende* or zinc sulphide (ZnS), and *red zinc ore*, in which zinc oxide (ZnO) is associated with the oxides of iron and manganese.

Calamine is so called from its tendency to form masses resembling a bundle of reeds (*calamus*, a reed). It is found in considerable quantities in Somersetshire, Cumberland, and Derbyshire. A compound of zinc carbonate with zinc hydroxide $ZnCO_3.2Zn(OH)_2$, is found abundantly in Spain. The mineral known as *electric calamine* (*hemimorphite*) is a silicate of zinc ($2ZnO.SiO_2.H_2O$), which becomes electrified when heated. Blende derives its name from the German *blenden*, to dazzle, in allusion to the brilliancy of its crystals, which are generally almost black from the presence of iron sulphide, the true colour of pure zinc sulphide being white. Blende is found in Cornwall, Cumberland, Derbyshire, Wales, and the Isle of Man, and is generally associated with galena or lead sulphide, which is always carefully picked out of the ore before smelting it, since it would become converted into lead oxide, which corrodes the earthern retorts employed in the process.

Before extracting the metal from these ores, they are subjected to a preliminary treatment which brings them both to the condition of zinc oxide. For this purpose the calamine is simply calcined in a reverberatory furnace, in order to expel carbonic acid gas; but the blende is *roasted* for ten or twelve hours, with constant stirring, so as to expose fresh surfaces to the air, when the sulphur passes off in the form of SO_2, and its place is taken by the oxygen, the ZnS becoming ZnO. The extraction of the metal from this zinc oxide depends upon the circumstance that zinc is capable of being distilled at a bright red heat, its boiling-point being about 930° C.

The facility with which this metal passes off in the form of vapour is seen when it is melted in a ladle over a brisk fire, for at a bright red heat abundance of vapour rises from it, which, taking fire in the air, burns with a brilliant greenish-white light, throwing off into the air, numerous white flakes of light zinc oxide (the *philosopher's wool*, or *nil album* of the old chemists).

* The sal ammoniac acts upon the heated zinc according to the equation, $Zn + 2NH_4Cl = ZnCl_2 + 2NH_3 + H_2$, and the zinc chloride which is formed dissolves the oxide from the surface of the metal, producing zinc oxychloride.

The distillation of zinc may be effected on the small scale in a black-lead crucible (A, Fig. 215) about 5 inches high and 3 in diameter. A hole is drilled through the bottom with a round file, and into this is fitted a piece of wrought-iron gas-pipe (B) about nine inches long and 1 inch wide, so as to reach nearly to the top of the inside of the crucible. Any crevices between the pipe and the sides of the hole are carefully stopped up with fireclay moistened with solution of borax. A few ounces of zinc are introduced into the crucible, the cover of which is then carefully cemented on with fireclay (a little borax being added to bind it together at a high temperature), and the hole in the cover is stopped up with fireclay. The crucible having been kept for several hours in a warm place, so that the clay may dry, it is placed in a cylindrical furnace with a hole at the bottom, through which the iron pipe may pass, and a lateral opening, into which is inserted an iron tube (C) connected with a forge bellows. Some lighted charcoal is thrown into the furnace, and when this has been blown into a blaze, the furnace is filled up with coke broken into small pieces. The fire is then blown till the zinc distils freely into a vessel of water placed for its reception. Four ounces of zinc may be easily distilled in half an hour.

The original *English method* for extracting zinc from the roasted ores consisted in mixing the ground ore with about half its weight of coke, and strongly heating the mixture in crucibles provided with tubes, like that shown in Fig. 215; the zinc was thus distilled *per descensum* in the manner described in the preceding paragraph. The reduction of zinc oxide by carbon is represented by the equation $ZnO + C = Zn + CO$.

Fig. 215.
Distillation of zinc.

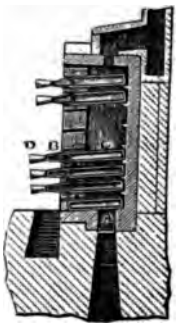


Fig. 216.
Belgian zinc furnace.

This reaction is found to be endothermic when its thermal value is calculated from ordinary data (see p. 307), which will account for the very high temperature (1300° C.) required to effect the reduction; this is probably aided by the volatility of zinc, which escapes from the sphere of action as soon as it is liberated, and allows a mass action of the carbon to come into play (see p. 310).

At the present day the reduction and distillation of zinc is effected in retorts, which are either of the *Belgian* or the *Silesian* type; the construction of each will be understood from the accompanying figures.

At Liége, in Belgium, calamine is exposed to the rain for several months in order to wash out the clay; it is then calcined and mixed with half its weight of coal-dust, and distilled in cylindrical fireclay retorts (C, Fig. 216), holding about 40 lbs. each, and set in seven tiers of six each in the same furnace, the vapour of zinc being conveyed by a short conical iron pipe (B) into a conical iron receiver (D), which is emptied every two hours into a large ladle, from which the zinc is poured into ingot moulds. Each distillation occupies about twelve hours. The advantage of this particular mode of arranging the cylinders is, that it economises fuel by allowing the poorer ores, which require less heat to distil all the zinc from them, to be introduced into the upper rows of cylinders farthest from the fire (A). There are two varieties of Belgian ore, one containing 33 and the other 46 per cent. of zinc, but a large proportion of this is in the form of silicate, which is not extracted by the distillation.

In Silesia the zinc oxide is mixed with fine cinders, and distilled in arched

earthen retorts (A, Fig. 217), into which the charge is introduced through a small door (B), which is then cemented up. The retorts are arranged in a double row in the same furnace (Fig. 218), and the vapour of zinc is condensed in a bent earthenware pipe attached to each retort, and having an opening (C) near the bend, which is kept closed, unless it is necessary to clear out the pipe.

The Silesian zinc is remelted, before casting into ingots, in clay instead of iron pots, since melted zinc always dissolves iron, and a very small quantity of that metal is found to injure zinc when required for rolling into sheets.

Fig. 217.

A small quantity of lead always distils over together with the zinc, and since this metal also interferes with the rolling of zinc into sheets, a portion of it is separated from zinc intended for this purpose, by melting the *spelter*, in large quantity, upon the hearth of a reverberatory furnace, the bed of which is inclined so as to form a deep cavity at the end nearest the chimney. The specific gravity of lead being 11.4, whilst that of zinc is 7, the former accumulates chiefly at the bottom of the cavity, and the ingots cast from the upper part of the melted zinc will contain but little lead, since zinc is not able to dissolve more than 1.5 per cent. of that metal at 400° C.

Fig. 218.—Silesian zinc furnace.

The electrolytic extraction of zinc is said to be practised at some places. By one process the roasted ore is leached with dilute sulphuric acid which dissolves the zinc oxide as sulphate; the solution is passed over metallic zinc to deposit other metals electro-negative to zinc, and electrolysed with zinc cathodes and carbon anodes. The zinc is deposited on the former, and oxygen evolved at the latter, dilute H_2SO_4 being left in the liquid to be used to leach more ore.

Ingots of zinc, when broken across, exhibit a beautiful crystalline fracture, which, taken in conjunction with the bluish colour of the metal, enables it to be easily identified. The spelter of commerce is liable to contain lead, iron, tin, antimony, arsenic, copper, cadmium, magnesium, and aluminium. Belgian zinc is usually purer than the English metal.

Zinc being easily dissolved by diluted acids, it is necessary to be careful in employing this metal for culinary purposes, since its soluble salts are poisonous.

It will be remembered that the action of diluted sulphuric acid upon zinc is employed for the preparation of hydrogen. Pure zinc, however, evolves hydrogen very slowly, since it becomes covered with a number of hydrogen bubbles which protect it from further action; but if a piece of copper or platinum be made to touch the zinc beneath the acid, these metals, being electro-negative towards the zinc, will attract the electro-positive hydrogen, leaving the zinc free from bubbles, and exposed on all points to the action of the acid, so that a continuous dis-

engagement of hydrogen is maintained. As a curious illustration of this, a thin sheet of platinum or silver foil may be shown to sink in diluted sulphuric acid, until it comes in contact with a piece of zinc, when the bubbles of hydrogen bring it up to the surface. The lead, iron, &c., met with in commercial zinc, are electro-negative to the zinc, and thus serve to maintain a constant evolution of hydrogen.

Zinc also dissolves in boiling solutions of potash and soda, evolving hydrogen; $2KOH + Zn = Zn(OK)_2 + H_2$. Even solution of ammonia dissolves it slowly. When heated with $Ca(OH)_2$ it evolves hydrogen.

A coating of metallic zinc may be deposited upon copper by slow galvanic action, if the copper be immersed in a concentrated solution of potash, at the boiling-point of water, in contact with metallic zinc, when a portion of the latter is dissolved in the form of oxide, with evolution of hydrogen, and is afterwards precipitated, on the surface of the copper.

Zinc-dust is metallic zinc which has condensed in a fine powder in smelting the ores. It is very useful in the laboratory as a reducing-agent.

Zinc oxide (ZnO).—Zinc forms but one oxide, which is known in commerce as *zinc-white* or *Chinese white*, and is prepared by allowing the vapour of the metal to burn in earthen chambers through which a current of air is maintained. It is practically insoluble in water, and is sometimes used for painting in place of white lead (basic lead carbonate), over which it has the advantages of not injuring the health of the persons using it, and of being unaffected by sulphuretted hydrogen, an important consideration in manufacturing towns where that substance is so abundantly supplied to the atmosphere. Unfortunately, however, the zinc oxide paint has less covering power and is more liable to peel off than white lead paint. The zinc oxide has the characteristic property of becoming yellow when heated, and white again as it cools. Its sp. gr. is 5.6. It is sometimes used in the manufacture of glass for optical purposes. At the temperature of the electric arc it is volatile.

Zinc hydroxide, $Zn(OH)_2$, is precipitated in a gelatinous state when caustic alkalies are added to solutions containing zinc; the precipitate dissolves in the excess of alkali, and, if this be not too great, is reprecipitated by boiling. The alkaline solution is said to contain an *alkali zincate*, *e.g.*, K_2ZnO_2. Ammonia does not precipitate zinc hydroxide from solutions containing ammonium salts, since zinc resembles magnesium in forming double salts containing ammonium. Zinc hydroxide is easily decomposed by heat; $Zn(OH)_2 = ZnO + H_2O$.

Zinc nitride, Zn_3N_2.—When zinc ethide (see *Organo-mineral Compounds*) is acted on by ammonia, it is converted into *zinc-diamine*; $Zn(C_2H_5)_2 + 2NH_3 = Zn(NH_2)_2 + 2C_2H_6$ (*ethyl hydride*). When zinc-diamine is heated, out of contact with air, it gives zinc nitride; $3Zn(NH_2)_2 = Zn_3N_2 + 4NH_3$. The nitride decomposes with water, evolving much heat; $Zn_3N_2 + 3H_2O = 2NH_3 + 3ZnO$.

Zinc carbonate, $ZnCO_3$, as found in nature (*calamine*, *Smithsonite*) forms rhombohedral crystals. The place of part of the zinc in the mineral is often taken by isomorphous metals, such as cadmium, magnesium, and ferrous iron. $ZnCO_3$ is precipitated when $ZnSO_4$ is boiled with $KHCO_3$; $ZnSO_4 + 2KHCO_3 = ZnCO_3 + K_2SO_4 + H_2O + CO_2$. The normal alkali carbonates precipitate basic carbonates of variable composition (as is the case with magnesium). The precipitate produced by ammonium carbonate is soluble in excess.

Zinc chloride, $ZnCl_2$ (= 136.5 = 2 volumes), is prepared by dissolving Zn or ZnO in HCl, and evaporating*. If the solution contains a little

* If iron be present, it may be separated by adding a little chlorine water to peroxidise it, and precipitating it as hydrated Fe_2O_3 by adding zinc carbonate.

HCl in excess, it deposits octahedral crystals of $ZnCl_2.H_2O$. The solution, like that of $MgCl_2$, undergoes partial decomposition when evaporated leaving an oxychloride; when this residue is distilled, $ZnCl_2$ passes over. It may also be obtained by distilling a mixture of zinc sulphate and sodium chloride. Zinc chloride is a deliquescent solid, very soluble in water, alcohol, and ether; it melts at 250° C. and boils at 730° C. Its attraction for water renders it a powerful caustic, and it is used as such in surgery. A strong solution of $ZnCl_2$ dissolves much ZnO, and if the solution of *oxychloride* thus formed be mixed with water, precipitates are obtained which contain Zn(OH)Cl and $Zn(OH)_2$. Solution of $ZnCl_2$ dissolves paper and cotton, and the oxychloride dissolves wool and silk. This is sometimes useful in examining textile fabrics.

When zinc oxide is moistened with a strong solution of zinc chloride, an oxychloride is formed, which soon sets into a hard mass, forming a very useful stopping for teeth.

Burnett's disinfecting fluid is a solution of zinc chloride, and is capable of absorbing H_2S, NH_3, and other offensive products of putrefaction, as well as of arresting the decomposition of wood and animal substances. Zinc chloride is also used in soldering, to cleanse the metallic surface, and the careless use of this poisonous salt in soldering tins of preserved food has frequently caused accidents.

Zinc chloride is sometimes made from pyrites containing blende. This is burnt as usual to furnish SO_2 for the manufacture of sulphuric acid, when the ZnS is converted into $ZnSO_4$ which is extracted from the spent pyrites by water, and decomposed with sodium chloride, when Na_2SO_4 is deposited in crystals, leaving $ZnCl_2$ in solution.

Zinc sulphate, or *white vitriol*, $ZnSO_4.H_2O.6Aq$, bears a dangerous resemblance to Epsom salts, but it loses its water of crystallisation at 100° C., and is decomposed at a very high temperature into ZnO, sulphur dioxide, and oxygen, whereas $MgSO_4$ bears fusion without being decomposed. Hence $ZnSO_4$, when heated to redness, leaves a residue which is yellow when hot and white when cold.

At temperatures above 40° C. zinc sulphate crystallises as $ZnSO_4.H_2O.5Aq$. which is isomorphous with the corresponding salt of magnesium. Like the magnesium sulphate, it forms double sulphates, in which the H_2O is exchanged for alkali sulphates. $ZnSO_4.K_2SO_4.6Aq$ and $ZnSO_4.(NH_4)_2SO_4.6Aq$ are isomorphous with the Mg double salts. Like all other truly isomorphous salts, the sulphates of magnesium and zinc crystallise together from their mixed solutions.

It is made on the large scale by roasting blende (zinc sulphide, ZnS) at a low red heat, when it combines with O from the air to form $ZnSO_4$, which is dissolved out by water and crystallised. It has a metallic, nauseous taste, and is used medicinally and in dyeing.

Zinc sulphide, ZnS, as found native, is usually crystallised in octahedra or dodecahedra, coloured black by ferrous sulphide (*black Jack*). Pale yellow specimens are sometimes found. When precipitated by a soluble sulphide from a solution of a zinc salt it is perfectly white, but it darkens somewhat when exposed to air and light.

An intimate mixture of zinc-dust with half its weight of flowers of sulphur burns like gunpowder when kindled with a match, leaving a bulky mass of ZnS, which is primrose-yellow while hot, and white on cooling. Zinc sulphide is insoluble in water, in alkalies, and in acetic acid, but dissolves in HCl and in HNO_3. It may be sublimed in colourless crystals by strongly heating in a current of H_2S.

Zinc silicate is found as *electric calamine*, $Zn_2SiO_4.Aq$, in rhombic crystals. *Zinc phosphate* forms the mineral *hopeite*, $Zn_3(PO_4)_2.4Aq$.

Zinc differs from all the other common metals in being precipitated as a white sulphide.

CADMIUM.

Cd″ = 111.6 parts by weight = 2 vols.

203. This metal is found in small quantities in the ores of zinc, its presence being indicated during the extraction of that metal (p. 378) by the appearance of a brown flame (*brown blaze*) at the commencement of the distillation, before the characteristic zinc flame is seen at the orifice of the receiver. Cadmium is more easily vaporised than zinc, boiling at 778° C., so that the bulk of it is found in the first portions of the distilled metal, If the mixture of cadmium and zinc be dissolved in diluted sulphuric acid, and the solution treated with hydrosulphuric acid gas, a bright yellow precipitate of *cadmium sulphide* (CdS) is obtained, which is employed in painting under the name of *cadmia* or *cadmium yellow*.* By dissolving this in strong hydrochloric acid and adding ammonium carbonate, cadmium carbonate ($CdCO_3$) is precipitated from which metallic cadmium may be extracted by distillation with charcoal.

Although resembling zinc in its volatility and its chemical relations, in appearance it is much more similar to tin, and emits a crackling sound like that metal when bent. Like tin, also, it is malleable and ductile at the ordinary temperature, and becomes brittle at about 82° C. Cadmium is slightly heavier than zinc, sp. gr. 8.6, and has a lower melting-point, 320° C., so that it is useful for making fusible alloys. An alloy of 3 parts of cadmium with 16 of bismuth, 8 of lead, and 4 of tin, fuses at 60° C. In its behaviour with acids and alkalies cadmium is similar to zinc, but the metal is easily distinguished from all others by its yielding a characteristic chestnut-brown oxide when heated in air. This oxide (CdO) is the only oxide of cadmium.

An amalgam of cadmium and mercury is used by dentists for stopping teeth, for while it is plastic when freshly made it rapidly hardens. It is also electro-deposited as an alloy with silver instead of ordinary electro-plating.

Cadmium chloride, $CdCl_2.2Aq$, effloresces in air, whilst zinc chloride deliquesces. Moreover, it may be dried without undergoing partial decomposition. It is fusible and volatile like zinc chloride. *Cadmium bromide*, $CdBr_2.4Aq$, and the *iodide*, CdI_2, are used in photography. *Cadmium sulphate*, $3CdSO_4.8Aq$ is much less soluble than zinc sulphate.

Cadmium differs from all the other metals in forming a *yellow* sulphide insoluble in alkalies, so that its salts, mixed with excess of ammonia, and treated with H_2S, give a yellow precipitate.

BERYLLIUM, OR GLUCINUM.

Be″ or Gl″ = 9 parts by weight.

204. This comparatively rare metal (which derives its name from the sweet taste of its salts, γλυκύς, sweet) is found associated with silica and alumina in the *emerald*, which is a double silicate of Al_2O_3 and BeO ($Al_2O_3.3BeO.6SiO_2$), and

* The darker varieties of this pigment contain thallium.

appears to owe its colour to the presence of a minute quantity of chromium oxide. The more common mineral *beryl* or *aquamarine*, has a similar composition, but is of a paler green colour, apparently caused by iron. *Chrysoberyl* consists of $Al_2O_3.BeO$, also coloured by iron. The earlier analysts of these minerals mistook the beryllium oxide for alumina, which it resembles in forming a gelatinous precipitate on adding ammonia to its solutions, but it is a stronger base than alumina, and is therefore capable of displacing ammonia from its salts, and of being dissolved by them. Ammonium carbonate is employed to separate the beryllium oxide from alumina, since it dissolves the former in the cold, forming a double carbonate of beryllium and ammonium, from which the beryllium carbonate is precipitated on boiling. Beryllium oxide, BeO, is intermediate in properties between alumina and magnesia, resembling the latter in its tendency to absorb carbonic acid from the air, and to form soluble double salts with the salts of ammonium, and so much resembling alumina in the gelatinous form of its hydrate, its solubility in alkalies, and the sweet astringent taste of its salts, that it was formerly regarded as a sesquioxide like alumina. By the *radiant matter test* (p. 330), beryllium oxide phosphoresces of a bright blue colour.

The metal itself is very similar to aluminium; it is prepared by passing the vapour of its chloride, $BeCl_2$, over melted sodium. Its sp. gr. is 1.6, and it melts at about 1000° C. It is not seriously oxidised by air and decomposes hot water very slowly.

General review of the magnesium group of metals.—This group includes Be, Mg, Zn, Cd and Hg. As in the case of the preceding groups of metals, the melting-point falls with the rise of atomic weight (Hg = 200 melts at − 36° C.), whilst the specific gravity and atomic volume (p. 304) rise with the atomic weight (sp. gr. Hg = 13.5).* Their order of chemical energy, on the other hand, is the reverse of that of the metals of the preceding groups, falling with rise of atomic weight. Their oxides are practically insoluble in water, and are less basic as the molecular weight increases. The carbonates are easily decomposed by heat; the sulphates are more easily decomposed than those of the metals of the preceding groups and appear to decrease in stability with rise of molecular weight. The vapours of these metals contain monatomic molecules (p. 300).

Mercury will be considered later.

ALUMINIUM.

$Al''' = 27$ parts by weight.

205. Aluminium is distinguished among metals, as silicon is among non-metallic bodies, for its immense abundance in the solid mineral portion of the earth, to which, indeed, it is almost entirely confined, for it is present in vegetables and animals in so small a quantity that it can scarcely be regarded as forming one of their necessary components. Church has, however, found it in certain cryptogamous plants, especially in the Lycopodiums; the ash of *Lycopodium alpinum* yielding one-third of its weight of alumina.

One of the oldest rocks, which appears to have originally formed the basis of the solid structure of the globe, is that known as *granite*. This mineral, which derives its name from its conspicuous *granular* structure, is a mixture, in variable proportions, of quartz, felspar, and mica, tinged of various colours by the presence of small quantities of the oxides of iron and manganese.

Quartz, which forms the translucent or transparent grains in the

* The atomic volume of Mg is greater than that of Zn.

granite, consists simply of silica; *felspar*, the dull, cream-coloured, opaque part, is a combination of silica with oxides of aluminium and potassium, of the composition $K_2O.3SiO_2.Al_2O_3.SiO_2$.

Mica, so named from the *glittering* scales which it forms in the granite, is also a double silicate of alumina and potash, $K_2O.3Al_2O_3.4SiO_2$, but the Al_2O_3 is very frequently displaced by Fe_2O_3 and the K_2O by MgO.

By the long-continued action of air and water, the granite is gradually crumbled down or disintegrated, an effect which must be ascribed to a concurrence of mechanical and chemical causes. Mechanically, the rock is continually worn down by variations of temperature, and by the congelation of water within its minute pores, the rock being gradually split by the expansion attendant upon such congelation. Chemically, the action of water containing carbonic acid would tend to remove the potash from the felspar and mica in the form of carbonate of potash, whilst the silicate of alumina and the quartz would subsequently be separated by the action of water; the former being so much lighter, would be soon washed away from the heavy quartz, and, when again deposited, would constitute *clay*, the purest form of which is *kaolin* ($Al_2O_3.2SiO_2.2H_2O$).

Although clay, therefore, always consists mainly of silicate of alumina, it generally contains some uncombined silicic acid, together with variable proportions of lime, of oxide of iron, &c., which give rise to the numerous varieties of clay. Thus a pure Chinese kaolin will contain, per cent.—

SiO_2	Al_2O_3	H_2O	Fe_2O_3	MgO	Alkalies
50.5	33.7	11.2	1.8	0.8	1.9

whilst Stourbridge fireclay will contain about 85 per cent. of this *clay-substance* and some 15 per cent. of silica as quartz.

The silicate of alumina also constitutes the chief portion of several other very important mineral substances, among which may be mentioned *slate*, *fuller's earth*, and *pumice-stone*. *Marl* is clay containing a considerable quantity of carbonate of lime. *Loam* is also an impure variety of clay. The different varieties of *ochre*, as well as *umber* and *sienna*, are simply clays coloured by the oxides of iron and manganese.

Notwithstanding the abundance of aluminium in the form of clay, it is only comparatively recently that the metal has been extracted in quantity sufficient to make it of practical importance. Originally the metal was prepared by fusing the chloride, preferably in the form of the double chloride, $Al_2Cl_6.2NaCl$, with sodium, which abstracted the chlorine. Now, however, aluminium is prepared by the electrolysis of a bath of fused cryolite (the double fluoride of aluminium and sodium, Na_3AlF_6), containing aluminium oxide (alumina, Al_2O_3), dissolved in it; the metal is deposited around the cathode, oxygen, and probably also fluorine, being evolved at the anode.

An iron box with double walls between which water is circulated has a steel plug protruding through its bottom; this plug serves as the cathode, the anode being a bundle of carbon rods suspended a short distance above the plug. At first an arc is struck between these electrodes and cryolite is fed into the vessel. As the cryolite melts the anode is drawn up and electrolysis begins, the bath being kept melted, by the heat generated by its electrical resistance, except the layer next the cooled walls of the vessel which are thus protected from the heat. Alumina is now fed into the

vessel in proportion as the aluminium separates around the cathode and is tapped off.

The alumina for this process is obtained from *bauxite*, a mineral found at Baux, near Arles in the South of France, and in Antrim, Ireland. It contains alumina 56 per cent., ferric oxide 3, silica 12, titanic acid 3, and water 26. To obtain alumina from it, it is roasted to oxidise any organic matter and ferrous oxide, and heated under pressure with caustic soda solution whereby the alumina is dissolved as sodium aluminate, $3Na_2O.Al_2O_3$. After filtration a small proportion of alumina is added to the liquid and the whole is agitated. In the course of some hours the greater part of the alumina is deposited from the solution, recalling the separation of a salt from a supersaturated solution by addition of a nucleus. The liquor from which the alumina has been separated is used for extracting another portion of the ignited bauxite. The deposited alumina is filtered, washed, and heated to expel water.

Aluminium is less fusible than tin and zinc, but more so than silver, its fusing-point being 655° C.* It requires a very high temperature to vaporise it. Like zinc, it is most easily rolled and bent between 100° and 150° C. It is much more sonorous than most other metals. A bar of it suspended from a string, and struck with a hammer, emits a clear musical sound. It is remarkable as being the lightest metal (sp. gr. 2.7) capable of resisting the action of air even in the presence of moisture. This lightness renders it valuable for the manufacture of small weights, such as the grain and its fractions, since these, when made of aluminium, are more than three times as large as when made of brass, and nearly nine times as large as platinum weights of the same denomination; and for canteen vessels, for which purpose it is applicable since it is sufficiently resistant to the attack of vegetable and animal juices.† It is also employed for ornamental purposes, for, though not so brilliant as silver, it is not blackened by sulphuretted hydrogen, which so easily affects that metal (see p. 215). Aluminium leaf has largely displaced silver leaf as a decorative material, and is capable of being printed on fabrics. Iron and silicon are the chief impurities in commercial aluminium.

Another characteristic feature of aluminium is its comparative resistance to the action of nitric acid even at a boiling heat. No other metal commonly met with, except platinum and gold, is capable of resisting the action of nitric acid to the same extent. Hydrochloric acid, however, which will not attack gold and platinum, dissolves aluminium with facility, converting it into aluminium chloride, with disengagement of hydrogen; $Al_2 + 6HCl = Al_2Cl_6 + H_6$. Solutions of potash and soda also easily dissolve it, forming the so-called aluminates of those alkalies; thus, $6NaOH + Al_2 = Al_2(ONa)_6 + H_6$. Even when very strongly heated in air, aluminium is oxidised to a very slight extent, probably because the coating of alumina which is formed remains infusible and protects the metal beneath it. For a similar reason, apparently, aluminium decomposes steam but slowly, even at a high temperature.

When aluminium is rubbed with a solution of mercuric chloride it becomes amalgamated with mercury on the surface and is then remarkably active, decomposing water at the ordinary temperature with violence, and serving as a useful neutral reducing-agent.

* It is not easily fused before the blowpipe, as its surface becomes covered with infusible oxide.

† The metal is not easily soldered and many alloys have been suggested for the purpose; of late one containing 1 of Al, 0.1 of P, 8 of Zn and 30 of Sn has been used.

Although massive aluminium does not oxidise more than superficially when heated, the powdered metal burns with ease like powdered magnesium. The heat of combustion is $Al_2O_3 = 360{,}000$ cals., and the temperature produced is very high. Indeed, if the oxygen be supplied by an admixture of a metallic oxide the temperature becomes comparable with that of the electric arc, and even highly refractory metals are both reduced and melted when their oxides are mixed with powdered aluminium and the mixture is ignited.*

Metallic chromium has been produced in this manner. A mixture of ferric oxide and aluminium powder has been used under the name "thermite," for the production of local high temperatures; the mixture is ignited in a crucible by a fuse composed of a mixture of barium peroxide and aluminium powder and when the combustion is over the white hot molten iron with its superincumbent layer of molten aluminium is poured on to the surface to be heated, such as two rails which are to be butt-jointed by fusing the ends together. When the mixture is ignited on an iron plate it fuses its way through the metal.

When aluminium is fused with nine times its weight of copper, it forms an alloy (*aluminium bronze*) very similar to gold in appearance, but almost as strong as iron. This alloy was strongly recommended as a substitute for gold for ornamental purposes, but it does not retain its brilliancy so completely as that metal. Aluminium does not dissolve in cold mercury nor in melted lead, both of which are capable of dissolving nearly all other metals.

An alloy of aluminium with from 10 to 25 per cent. of magnesium is sold as "magnalium"; it is of lower specific gravity than aluminium and is more easily worked.

Aluminium is also used for reducing any oxide which may be present in molten steel when it is being cast, a small amount being added to the steel just before it is poured.

206. **Alum,** which is the chief compound of aluminium employed in the arts, is always obtained either from clay or slate, but there are several processes by which it may be manufactured.

The simplest process is that in which pipe-clay, or some other clay containing very little iron, is calcined, ground to powder, and heated on the hearth of a reverberatory furnace with half its weight of sulphuric acid, until it becomes a stiff paste, which is then exposed to air for several weeks. During this time the alumina of the clay is attacked by the sulphuric acid to form aluminium sulphate, which may be obtained by washing the mass with water, when the sulphate dissolves, and the undissolved silica (still retaining a portion of the alumina) is left. When the solution containing the aluminium sulphate is evaporated to a syrupy consistence and allowed to cool, it solidifies into a white crystalline mass, which is used by dyers under the erroneous name of *concentrated alum* or *cake-alum*, and contains about 47.5 per cent. of the dry salt. The *aluminium sulphate* can be obtained in crystals containing $Al_2(SO_4)_3.18Aq$,† but there is considerable difficulty in obtaining these crystals on account of the extreme solubility of the salt. It is on account of this circumstance that the aluminium sulphate is usually converted into alum, which admits of very easy crystallisation

* A mixture of aluminium powder and sodium peroxide ignites spontaneously when moistened.

† The mineral *alunogen* found in New South Wales has this composition (Liversidge). It forms fibrous masses like satin-spar, and occurs in sandstone rocks.

and purification. In order to transfer the sulphate into alum, its solution is mixed with potassium sulphate, when, by suitable evaporation, beautiful octahedral crystals are obtained, having the composition $AlK(SO_4)_2.12Aq$.*

Alum is more commonly prepared from the mineral termed *alum shale*, which contains silicate of alumina, together with a considerable quantity of finely divided iron pyrites and some bituminous matter. This shale is coarsely broken up, and built into long pyramidal heaps, together with alternate layers of coal, unless the shale should happen to contain a sufficient amount of bitumen. These heaps are kindled in several places, and are partly smothered with spent ore in order to prevent too great a rise of temperature. During this slow roasting of the heap, the iron pyrites (FeS_2) loses half its sulphur, which is converted by burning into sulphurous acid gas (SO_2), and this, in contact with the porous shale and the atmospheric oxygen, becomes converted into SO_3 (p. 222). This latter combines with the alumina to produce sulphate of alumina. The roasted heap is then allowed to remain for some months exposed to the air, and moistened from time to time, in order to promote the absorption of oxygen by the sulphide of iron (FeS), and its conversion into sulphate of iron ($FeSO_4$). This heap is afterwards lixiviated with water, which dissolves out the sulphates of aluminium and iron, together with some magnesium sulphate, which has also been formed in the process. When this *crude alum liquor* is evaporated to a certain extent, a large quantity of ferrous sulphate (green vitriol) crystallises out, and the liquid from which these crystals have separated is then mixed with so much solution of potassium chloride as a preliminary experiment has shown to be necessary to yield the largest amount of alum. The potassium chloride is obtained either from Stassfurt, or as soap-boiler's waste, or as the refuse from saltpetre refineries and glass-houses. The ferrous sulphate still left in the solution is decomposed by the potassium chloride, yielding ferrous chloride, and potassium sulphate, which combines with the aluminium sulphate to form alum; (1) $FeSO_4 + 2KCl = K_2SO_4 + FeCl_2$; (2) $K_2SO_4 + Al_2(SO_4)_3 = 2KAl(SO_4)_2$. The hot liquor is stirred while cooling, when *alum meal* is deposited in small crystals, and the $FeCl_2$ remains in solution. The alum is redissolved in boiling water, and crystallised in barrels, which are taken to pieces to get out the large crystals. If there be much magnesium sulphate in the liquor, it is subsequently obtained in crystals and sent into the market.

Where ammonium sulphate can be obtained at a cheap rate (as in the neighbourhood of gasworks), it is very commonly substituted for the potassium sulphate, when *ammonia-alum* is obtained instead of *potash-alum*. The former is similar in all respects to the latter salt, except that it contains the hypothetical metal ammonium (NH_4) in place of potassium, and its formula is therefore $AlNH_4(SO_4)_2.12$ Aq.

For all the uses of alum, in dyeing and calico-printing, in paper-making, and in the manufacture of colours, ammonia-alum answers quite as well as potash-alum, and hence both these salts are sold under the common name of alum.

These alums are the representatives of an important class of double sulphates, containing a monatomic and a triatomic metal. They all contain 12 molecules of water of crystallisation, and their crystalline form is that of the cube or octahedron. Alum dissolves in one-third of its weight of boiling water, and in seven parts of cold water; it is insoluble in alcohol. When heated, it fuses and swells up to a light porous mass of *burnt alum*, having lost its water.

The solution of alum is acid to test-papers. When solution of

* When a supersaturated solution (p. 51) of these crystals is concentrated in a flask, stoppered with cotton-wool, until a film of solid appears on the surface of the liquor, the solution sets, on cooling, to a mass of prismatic crystals. By carefully removing the cotton-wool and introducing a crystal of the ordinary, octahedral alum, the whole of the already solidified substance may be made to break up, the prismatic crystals being transformed into the octahedral variety, with much evolution of heat.

sodium carbonate is added to it by degrees, a precipitate of aluminium hydroxide is formed, which, at first, is redissolved on stirring. The solution, to which sodium carbonate has been added as long as the precipitate redissolves, is used under the name of *basic alum* in dyeing, because stuffs immersed in it become impregnated with alumina, which serves as a mordant to attract and fix the colouring-matter when the stuff is transferred to a dye-bath.

Aluminium sulphate is superseding alum in many applications; being prepared by treating clay or bauxite (see p. 385) with sulphuric acid, and precipitating the iron either as ferric arsenate or as Prussian blue.

Alumina.—When ammonia-alum is strongly heated it leaves a white insoluble earthy substance which is alumina itself (Al_2O_3), and differs widely from the metallic oxides which have been hitherto considered, by the feebly basic character which it exhibits.* Not only is alumina destitute of alkaline properties, but it is not even capable of entirely neutralising the acids, and hence both aluminium sulphate and alum are exceedingly acid salts. Indeed, alumina has feebly acid properties towards the powerful bases, forming *aluminates* such as sodium aluminate, $3Na_2O.Al_2O_3$.

Pure crystallised alumina is found in nature as the mineral *corundum*, distinguished by its extreme hardness, in which it ranks next to the diamond. An opaque and impure variety of corundum constitutes the very useful substance *emery*. The *ruby*, oriental amethyst, and *sapphire*† consist of nearly pure alumina; *spinelle* is a compound of magnesia with alumina, $MgO.Al_2O_3$; whilst in the *topaz* the alumina is associated with silica and aluminium fluoride. In these forms the alumina is insoluble in acids, but it may be rendered soluble by fusion with acid potassium sulphate, or with alkali hydroxides. The sp. gr. of alumina varies from 3.7 to 4.2.

The mineral *diaspore* is a hydrate of alumina ($Al_2O_3.2H_2O$), so named from its falling to powder when heated (*διασπορά, dispersion*).

Artificial corundum has been made by fusing alumina either in the electric furnace or by the combustion of aluminium (p. 386) and allowing the fused mass to cool.

Aluminium hydroxide, $Al_2(OH)_6$, is found crystallised as *hydrargillite*, or *Gibbsite*. Artificially prepared aluminium hydroxide is characterised by its gelatinous appearance. If a little alum be dissolved in warm water, and some ammonia added to the solution, the alumina will precipitate as a semi-transparent gelatinous mass of the hydrate $Al_2(OH)_6.2H_2O$. It is nearly insoluble in ammonia, but dissolves in potash and soda. Aluminium hydroxide may be obtained in solution in water by dissolving it in solution of Al_2Cl_6, and dialysing (see p. 278). It resembles solution of silicic acid in being very easily gelatinised. When washed and dried, the gelatinous hydroxide shrinks very much, and forms a mass resembling gum. The hydroxide has a great attraction for most colouring-matters, with which it forms insoluble compounds called *lakes*. Thus, if a solution of alum be mixed with infusion of *logwood*, and a little ammonia added, the aluminium hydroxide will form, with the colouring-matter, a purplish-red *lake*, which may be filtered off, leaving the solution colourless. This property is turned to advantage in calico-printing, where the compounds of alumina are largely used as mordants.

By the *radiant matter test* (p. 330) alumina phosphoresces crimson.

* The great absorption and disappearance of heat during the evaporation of the water and ammonia from this alum, has led to its employment for filling the space between the double walls of fire-proof safes, which may become red-hot outside, whilst the inside is kept below the scorching point of paper.

† Small crystals of alumina resembling natural sapphire have been obtained by the action of vapour of aluminium fluoride upon boric anhydride at a high temperature. By adding a little chromium fluoride, crystals similar to rubies and emeralds have been produced.

Aluminium chlorides, $AlCl_3$.—If the alumina obtained by calcining ammonia-alum be intimately mixed with charcoal, and strongly heated in an earthen tube or retort through which a stream of well-dried chlorine is passed, the oxygen of the alumina is abstracted by the charcoal, to form carbonic oxide, whilst the chlorine combines with the aluminium, yielding aluminium chloride, which passes off in vapour, and may be condensed, in an appropriate receiver, as a white crystalline solid; $Al_2O_3 + C_3 + Cl_6 = 2AlCl_3 + 3CO$.

$AlCl_3$ absorbs moisture from the air, and becomes partly decomposed into Al_2O_3 and HCl. By dissolving alumina in HCl and evaporating, needles of $AlCl_3.6H_2O$ are obtained, but they are decomposed, when heated, into Al_2O_3, 6HCl, and $9H_2O$. An impure solution of aluminium chloride is sold as a disinfectant under the name of *chloralum*.

Aluminium fluoride, AlF_3, occurs in *kryolite*, $3NaF.AlF_3$.

207. **Mineral silicates of alumina.**—Many of the chemical formulæ of minerals which contain silicates of alumina associated with the silicates of other metallic oxides, are complicated, from the circumstance that iron often takes the place of a part of the aluminium, which is possible because Fe_2O_3 is isomorphous with Al_2O_3, and therefore capable of taking its place without altering the crystalline form and general character of the mineral. In a similar manner, the other metals present in the mineral may be exchanged for isomorphous representatives; thus, there are two well-known felspars, potash-felspar (*orthoclase*) and soda-felspar (*albite*), having the formulæ $K_2O.Al_2O_3.6SiO_2$ and $Na_2O.Al_2O_3.6SiO_2$. These minerals are sometimes mingled in one and the same crystal (*potash-albite* or *pericline*) without bearing any definite equivalent proportion to each other; the formula of such a mineral would be written $(KNa)_2O.Al_2O_3.6SiO_2$. *Porphyry* has the same chemical composition as felspar.

Mica includes the two minerals *muscovite*, $K_2O.3Al_2O_3.4SiO_2$, and *biotite*, $3MgO.Al_2O_3.3SiO_2$.

Garnet is essentially a double silicate of alumina and lime, but often contains magnesium, iron, or manganese, in place of part of the calcium, and iron in place of part of the aluminium, being written $3[CaMgFeMn]O.[AlFe]_2O_3.3SiO_2$. This mineral is sometimes formed artificially in the slag of the iron blast-furnaces. *Chlorite* has the composition; $[6MgFe]O.[AlFe]_2O_3.3SiO_2.4H_2O$.

Basalt is a felspathic rock containing crystals of *augite* ($[Fe,Mg]O.SiO_2$) and magnetic oxide of iron. *Cyanite*, *kyanite*, or *disthene* is $Al_2O_3.SiO_2$; a crystal of this is said to point north and south when freely suspended.

Gneiss is chemically composed like granite, but the mica is arranged in regular layers. *Trap* rock contains felspar together with *hornblende*, $(\frac{1}{4}FeO.\frac{3}{4}MgO)SiO_2$. Hornblende is sometimes found in the place of mica in *syenitic granite*. *Lava*, from volcanoes, consists essentially of ferrous, calcium, and aluminium silicates; the presence of a considerable proportion of potassium and of phosphoric acid renders the soil formed by the weathering of lava very fertile.

Lapis lazuli, the valuable mineral which furnishes the natural ultramarine used in painting, consists chiefly of silica and alumina, which constitute respectively 45 and 25 per cent. of it, but there are also present 10 per cent. of soda, 6 per cent. of sulphuric acid, about 3 per cent. of sulphur, and a somewhat smaller quantity of iron, together with a variable proportion of lime. The cause of its blue colour is not understood, since neither of its predominant constituents is concerned in the production of such a colour in other cases. In consequence of the rarity of the mineral, the natural ultramarine has a very high price, but the *artificial ultra-*

marine is manufactured in very large quantities at a low cost, and forms a very good imitation.

One of the processes for preparing it consists in heating to bright redness in a covered crucible, for three or four hours, an intimate mixture of 100 parts of pure white clay (kaolin), 100 of dried carbonate of soda, 60 of sulphur, and 12 of charcoal. This would be expected to yield a mixture of silicate of soda, aluminate of soda, and sulphide of sodium, the two first being white, and the last yellow or brown, but the mass is found to have a *green* colour (*green ultramarine*). It is finely powdered, washed with water, dried, mixed with a fifth of its weight of sulphur, and gently roasted in a thin layer till the sulphur has burnt off, this operation being repeated, with fresh additions of sulphur, until the residue has a fine blue colour. In the opinion of some chemists, the presence of a small proportion of iron is essential to the blue colour, whilst others believe the colour to be due to sodium sulphide or thio-sulphate, or both.*

Ultramarine is a very permanent colour under ordinary conditions of exposure to the air and light, but acids bleach it at once, with separation of gelatinous silica and evolution of sulphuretted hydrogen. Blue writing paper is often coloured with ultramarine, so that its colour is discharged by acids falling upon it in the laboratory. Chlorine also bleaches ultramarine. Starch is often coloured blue with this substance.

Phosphate of alumina, or *aluminium phosphate*, $AlPO_4$, is found naturally in several forms. It occurs in large quantities in the West India Islands. *Turquoise* is a hydrated aluminium phosphate, owing its colour to the presence of oxide of copper.† *Wavellite* has the composition $3Al_2O_3.2P_2O_5.12H_2O$. None of the earlier analysts detected the phosphoric acid in this mineral, on account of the difficulty in separating it from the alumina, so that even in comparatively modern chemical works it is described as a hydrate of alumina.

A gelatinous precipitate of $AlPO_4$ is formed when Na_2HPO_4 is added to solution of alum. It is soluble in HCl and in potash, but insoluble in acetic acid, which distinguishes it from aluminium hydroxide.

208. **Pottery, Porcelain and Bricks.**—The manufacture of these articles is frequently termed the *clay industries*, since clay of one kind or another is the basis of the industry in each case: the subject is therefore conveniently considered as an appendix to the chemistry of aluminium compounds.

The manufacture of pottery obviously belongs to an earlier period of civilisation than that of glass, since the raw material, clay, would at once suggest, by its plastic properties, the possibility of working it into useful vessels, and the application of heat would naturally be had recourse to in order to dry and harden it. Indeed, at the first glance, it would appear that this manufacture, unlike that of glass, did not involve the application of chemical principles, but consisted simply in fashioning the clay by mere mechanical dexterity into the required form. It is found, however, at the outset that the name of *clay* is applied to a large class of minerals, differing very considerably in composition, and possessing in common the two characteristic features of plasticity and a predominance of aluminium silicate.

It has already been stated (page 384) that *kaolin* is a hydrated aluminium silicate, and it is from this material that the best variety of

* Heumann assigns to ultramarine the formula $2Na_2Al_2Si_2O_8.Na_2S_2$. Knapp attributes the blue colour to the presence of a modification of sulphur which is only blue when spread over a large surface; in this case acids would bleach the colour by destroying the surface. Potassium ultramarine, in which K takes the place of Na, is also blue, whilst silver ultramarine, in which Ag is substituted for the Na, is yellow.

† False or bone turquoise is fossil ivory, owing its colour to the presence of the natural blue phosphate of iron. *Redonda phosphate* consists chiefly of $AlPO_4$.

porcelain is made. This clay is eminently plastic, and can therefore be readily moulded, but when baked it shrinks very much, so that the vessels made from it lose their shape and often crack in the kiln. In order to prevent this, the clay is mixed with a certain proportion of sand, chalk, bone-ash, or heavy-spar; but another difficulty is thus introduced, for these substances diminish the tenacity of the clay, and would thus render the vessels brittle. A further addition must therefore be made of some substance which fuses at the temperature employed in baking the ware, and thus serves as a cement to bind the unfused particles of clay, &c., into a compact mass. Felspar (silicate of aluminium and potassium) answers this purpose; or carbonate of potassium or of sodium is sometimes added, to convert a portion of the silica into a fusible alkaline silicate. With a mixture of clay with sand and felspar (or some substitutes), a vessel may be moulded which will preserve its shape and tenacity when baked, and will be impervious to water if it have been "fired" at a temperature sufficiently high to fuse the felspar and *clinker* the ware throughout. This is the case with porcelain and stoneware; earthenware, on the other hand, is not clinkered throughout and must be waterproofed by the application of some easily-fusible material which shall form a glaze over the surface of the ware. Porcelain is generally glazed in order to present a perfectly smooth surface, unless *biscuit* ware is to be manufactured. A distinction is drawn between *hard* porcelain, the constituents of which are such that the ware is exceedingly infusible, and *soft* porcelain, which is far more easily fused. *Berlin hard porcelain* is made from a mixture of some 55 parts of kaolin, 22.5 of quartz, and 22.5 of felspar.

These materials are ground up with water before being mixed, and the coarser particles are allowed to subside; the creamy fluids containing the finer particles in suspension are then mixed in the proper proportions and allowed to settle; the paste deposited at the bottom is drained, thoroughly kneaded, and stored away for some months in a damp place, by which its texture is considerably improved, and any organic matter which it contains becomes oxidised and removed, the oxidation being effected partly by the sulphates present, which become reduced to sulphides. It is then moulded into the required forms, and dried by simple exposure to the air. The vessels are packed in cylindrical cases (*saggers*) of very refractory clay, which are arranged in a furnace or kiln of peculiar construction, and very gradually heated at about 800° C. When sufficiently baked, the *biscuit* porcelain has to be glazed, and great care is taken that the glaze may possess the same expansibility by heat as the ware itself, for otherwise it would crack in all directions as the glaze ware cooled. The glaze employed is a mixture of felspar, quartz, kaolin, marble, and broken porcelain very finely ground, and suspended in water. When the porous ware is dipped into this mixture, it absorbs the water, and retains a thin coating of the mixture of quartz and felspar upon its surface. It is now again fired, this time at 1700° C., when the glaze fuses, partly penetrating the ware, partly remaining as a varnish upon the surface.

When the ware is required to have some uniform colour, a mineral pigment capable of resisting very high temperatures is mixed with the glaze; but coloured designs are painted upon the ware after glazing, the ware being then baked a third time, in order to fix the colours. These colours are glasses coloured with metallic

oxides, and ground up with oil of turpentine, so that they may be painted in the ordinary way upon the surface of the ware; when the latter is again heated in the kiln the coloured glass fuses, and thus contracts firm adhesion with the ware.

Gold is applied either in the form of precipitated metallic gold, or of fulminating gold, being ground up in either case with oil of turpentine burnt in, and burnished.

English soft porcelain is made from Cornish clay mixed with ground flints, burnt bones, and sometimes a little sodium carbonate, borax, and binoxide of tin, the last improving the colour of the ware. It is glazed with a mixture of Cornish stone (consisting of quartz and felspar), flint, chalk, borax, and sometimes white lead to increase its fusibility.

Stone-ware is made from less pure materials, and is covered with a glaze of sodium silicate, in a very simple manner, by a process known as *salt-glazing*. The ware is coated with a thin film of sand by dipping it in a mixture of fine sand and water, and is then intensely heated in a kiln into which a quantity of damp salt is presently thrown. The water is decomposed, its hydrogen taking the chlorine of the salt to form hydrochloric acid, and its oxygen converting the sodium into soda, which combines with the sand to form sodium silicate; this fuses into a glass upon the surface of the ware.

Pipkins, and similar *earthenware* vessels, are made of common clay mixed with a certain proportion of marl and of sand. They are glazed with a mixture of 4 or 5 parts of clay with 6 or 7 parts of litharge. The colour of this ware is due to the presence of ferric oxide.

Bricks and tiles are also made from common clay mixed, if necessary, with sand; such common clay contains sufficient fusible material to sinter the bricks. These are very often grey, or blue, or yellow, before baking, and become red under the action of heat, since the iron, which is originally present as carbonate ($FeCO_3$), becomes converted into the red peroxide (Fe_2O_3) by the atmospheric oxygen.*

For the manufacture of the refractory bricks for lining furnaces, of glass-pots, crucibles for making cast-steel, &c., a pure, and therefore infusible, clay is employed, to which a certain quantity of broken pots of the same material is added, to prevent the articles from shrinking whilst being dried.

Dinas firebricks are made from a peculiar siliceous material found in the Vale of Neath, and containing alumina with about 98 per cent. of silica. The ground rock is mixed with 1 per cent. of lime and a little water before moulding. These bricks are expanded by heat, whilst ordinary firebricks contract.

Blue bricks are glazed by sprinkling with *iron scurf*, a mixture of particles of stone and iron produced by the wear of the siliceous grindstones employed in grinding gun-barrels, &c. When the bricks are fired, a glaze of silicate of iron is formed upon them.

Gallium.

$Ga''' = 69.5$.

209. This metal is found in very small quantities in certain ores of zinc, particularly in the blende from Bensberg, in the Pyrenees.

The powdered ore is treated with aqua regia, care being taken that the blende is in excess, so that the nitric acid may be destroyed as far as possible. Lumps of zinc are immersed in the cooled filtrate from the undissolved ore, whereupon all metals appreciably electro-negative to zinc are precipitated; the filtrate from these is mixed with more zinc and boiled for some hours so that the acid may be completely neutralised by the zinc and basic salts of Al, Zn and Ga precipitated. They

* The efflorescence frequently noticed on bricks consists mainly of sulphate and chloride of sodium, which existed in the original clay; the former salt is frequently formed when iron pyrites is a constituent of the clay.

are dissolved in HCl, ammonium acetate is added and the Ga and Zn are precipitated by H_2S. The sulphides are dissolved in HCl, H_2S is boiled off and a deficiency of Na_2CO_3 added to precipitate Ga (which is less basic than Zn) as carbonate. The carbonate is dissolved in H_2SO_4 and excess of NH_3 is added; Ga_2O_3 is precipitated, any ZnO present being soluble in NH_3. The precipitate is dissolved in KHO and the solution electrolysed to deposit Ga on the cathode.

Gallium is a hard white metal of sp. gr. 6 remarkable for its low fusing-point (30° C.), so that it melts with the heat of the hand. It will remain liquid when cooled far below this temperature, but solidifies when touched with a piece of the solid metal. It is not oxidised by dry air until heated nearly to redness, and the oxidation is then only superficial. Nitric acid scarcely attacks it in the cold, but dissolves it on heating. Hydrochloric acid dissolves it, with evolution of hydrogen. Potash has a similar action.

Gallium sesquioxide, Ga_2O_3, left on igniting the nitrate, is white. When heated in hydrogen, a part sublimes, and the rest is converted into a bluish grey substance, which appears to be *gallium oxide*, GaO. Two chlorides, $GaCl_2$ and $GaCl_3$, exist; they are very fusible, and deliquescent; they boil at 535° C. and 220° C. respectively. $GaCl_2$ is oxidised to $GaCl_3$ by potassium permanganate solution.

Gallium sulphate, $Ga_2(SO_4)_3$, is very soluble in water; the solution deposits a basic salt when boiled. It combines with ammonium sulphate to form an alum, the solution of which is also precipitated by boiling.

Ammonia precipitates solutions of gallium, but the precipitate is more easily soluble in excess than in the case of aluminium. Ammonium sulphide precipitates Ga_2S_3 only if zinc be present, when ZnS is precipitated at the same time. Potash gives a precipitate which dissolves easily in excess. Potassium ferrocyanide produces a white precipitate, similar to that yielded by zinc.

The most delicate test for gallium (which led to its discovery in 1875) is the production of two violet bands in the spectrum, when an induction spark passes from the positive terminal of a secondary coil to the surface of the solution under examination, into which the negative terminal of the coil is made to dip.

From the description of its properties, it will be seen that gallium bears considerable resemblance to aluminium.

INDIUM.

$In''' = 113.1$.

210. Indium was discovered (1863) with the help of the spectroscope, in a specimen of blende from Freiberg, and in some calamines. Its name refers to an indigo-blue line in the spectrum. It is a white malleable metal, and dissolves in hydrochloric acid. Its specific gravity is 7.42. Fusing-point, 176° C. Less easily vaporised than zinc or cadmium. Indium dissolves in HCl, forming $InCl_3$; in HNO_3, forming $In(NO_3)_3$; and in H_2SO_4, forming $In_2(SO_4)_3$, which crystallises with $9H_2O$, and forms an alum.

Ammonia produces, in solutions of indium, a white precipitate, $In(OH)_3$; insoluble in excess. Ammonium carbonate gives a precipitate soluble in excess and reprecipitated by boiling. When ignited, $In(OH)_3$ yields the sesquioxide, In_2O_3, which is brown when hot but yellow when cold. When this is heated in hydrogen, InO is produced. The chlorides, InCl, $InCl_2$, and $InCl_3$ have been prepared; they have all been volatilised. In_2S_3 is a yellowish precipitate thrown down by H_2S from feebly acid solutions of indium.

To extract indium from the Freiberg zinc, the metal is boiled with dilute sulphuric acid, employed in such quantity as to leave part of the zinc undissolved, together with indium and lead. The residue is dissolved in nitric acid, the lead and cadmium precipitated by hydrosulphuric acid, the latter expelled by boiling, and the oxide of indium precipitated from the solution by barium carbonate. When this precipitate is dissolved in hydrochloric acid, and excess of ammonia added, the white indium hydroxide is precipitated, and may be reduced by heating in hydrogen. At a bright red heat it burns with a violet blue flame, yielding In_2O_3.

211. **Review of the aluminium group of metals.**—This group comprises Al, Ga, In, and Tl (thallium = 204). The last-named bears the same relation to the other metals of the group as mercury bears to the other metals of the magnesium

group (p. 381). The melting-points of the metals of the Al group do not descend with the rise of atomic weight; it is true that Al, which has the lowest atomic weight, has the highest melting-point, but the remaining metals show a rise of melting-point for increase of atomic weight (Tl melts at 290° C.). The sp. gr. rises with the atomic weight (Tl has sp. gr. 11.9). As the atomic weight increases there is a tendency for the formation of stable oxides lower than that typical of the group (R_2O_3), and this typical oxide becomes less stable; this will be evident when the properties of thallium have been considered, a matter best postponed until lead has been treated of.

The metals in the odd series of this group (see table, p. 302) are the rare elements *scandium*, *yttrium lanthanum*, and *ytterbium*.

212. **Scandium** (Sc = 43.8) is the metal existing in the basic oxide *scandia*, Sc_2O_3, found in the mineral *gadolinite*, a mixture of silicates occurring at Ytterby, in Sweden. The oxide is infusible and insoluble in alkalies. The metal has not been isolated, but the atomic weight is deduced from the equivalent of the oxide. Mendeléeff prophesied the existence of a metal (ekaboron) whose oxide would have the properties since discovered for scandia (see p. 304).

213. **Yttrium** (Yt = 88.3) is the metal of the oxide *yttria*, Yt_2O_3, which is extracted from gadolinite and a similar mineral, *samarskite*. Its properties are not yet known. Yttria is a white oxide insoluble in alkalies and soluble in alkali carbonates. It has been recently shown to contain five or six oxides of basicity differing very slightly from its own, and separable by fractional precipitation; these may be identified by the difference between their radiant spectra (p. 330), though their spark-spectra are identical with that formerly ascribed to yttrium.

214. **Lanthanum** (La = 137) also occurs in gadolinite, but is more abundant in *cerite*, a mineral of the same type, also containing the metal cerium. The mixture of *lanthana*, La_2O_3, and ceria obtained from this mineral is converted into nitrates which are fractionally crystallised, when the lanthanum nitrate separates first. When this is ignited it is converted into oxide which may be dissolved in HCl, and the chloride thus prepared may be fused with potassium to yield the metal lanthanum. It is a white malleable metal (sp. gr. 6.16), decomposes hot water, and oxidises rapidly in air.

215. **Ytterbium** (Yb = 172).—This metal is only known as its oxide, Yb_2O_3, at present; this is extracted from gadolinite.

216. Besides the above oxides, several others have been described as obtainable from the gadolinite minerals—*e.g.*, *terbia*, *erbia*, *holmia*, *thulia*, *samaria*, and *didymia*. These *rare earths* have received much attention from the spectroscopist, to whom the evidence of their existence is due, and who is gradually arriving at the conclusion that they are of more complex composition than was at first supposed. They have also received much attention from those interested in incandescence gas lighting (p. 155).

For example, the metal *didymium*, which was originally regarded as a chemical unit yielding the oxides DiO, Di_2O_3, and Di_2O_5, has been shown to contain two constituents, *praseodymium* and *neodymium*. When the red-coloured didymium nitrate is fractionally crystallised, it yields two salts, one of which, the praseo-salt, is green, whilst the other, the neo-salt, is red. Solutions of these give different absorption spectra (p. 331), but when they are mixed the absorption spectrum characteristic of didymium nitrate is obtained.

217. For a detailed account of the rare earths the reader must consult a more exhaustive treatise than the present one. It is possible that when the elements contained in them have been isolated, these will be found to occupy the ninth series of the periodic table (p. 302).

IRON.

$Fe'' = 56$ parts by weight. $(Fe_2)^{vi} = 112$.

218. **This most useful of all metals is one of those most widely and abundantly diffused in nature. It is to be found in nearly all forms of rock, clay, sand and earth, its presence in these being commonly indicated by their colours, for iron is the commonest of natural mineral colouring ingredients. It is also found, though in small proportion, in plants, and in larger quantity in the bodies of animals, especially in the**

blood, which contains about 0·5 per cent. of iron in very intimate association with its colouring-matter.

But iron is very rarely found in the metallic state in nature, being almost invariably combined either with oxygen or sulphur.

Metallic iron is met with, however, in the *meteorites* or metallic masses, sometimes of enormous size, and of unknown origin, which occasionally fall upon the earth. Of these, iron is the chief component, but there are also generally present cobalt, nickel, chromium, manganese, copper, tin, magnesium, carbon, phosphorus, and sulphur.

The chief forms of combination in which iron is found in sufficient abundance to render them available as sources of the metal, are shown in the following table:

Ores of Iron.

Common Name.	Chemical Name.	Composition.
Magnetic iron ore . .	Ferroso-ferric oxide . . .	Fe_3O_4
Red hæmatite } . . Specular iron }	Ferric oxide	Fe_2O_3
Brown hæmatite . .	Ferric hydrate	$2Fe_2O_3.3H_2O$
Spathic iron ore . .	Ferrous carbonate . . .	$FeCO_3$
Clay ironstone . .	Ferrous carbonate with clay	
Blackband . . .	Ferrous carbonate with clay and bituminous matter	
Iron pyrites . . .	Bisulphide of iron . . .	FeS_2

These ores are frequently associated with extraneous minerals, some of the constituents of which are productive of injury to the quality of the iron. It is worthy of notice that scarcely one of the ores of iron is entirely free from sulphur and phosphorus, substances which will be seen to have a very serious influence on the quality of the iron extracted from the ores, and the presence of which increases the difficulty of obtaining the metal in a marketable condition.

The following table illustrates the general composition of the most important English ores of iron, with reference to the proportions of iron, and of those substances which materially influence the character of the iron extracted from the ore—viz., manganese (present as oxide or carbonate), phosphorus (present as phosphates), and sulphur (present as bisulphide of iron). The maximum and minimum quantities found in each ore are specified.

British Iron Ores.

In 100 Parts.	Iron.		Oxide of Manganese, MnO.		Phosphoric Anhydride, P_2O_5.		Bisulphide of Iron (Pyrites).		No. of Samples Analysed.
	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	
Clay ironstone from coal-measures	43.30	20.95	3.30	0.46	1.42	0.07	1.21	...	77
Clay ironstone from the lias . .	49.17	17.34	1.30	...	5.05	...	1.60	...	12
Brown hæmatite	63.04	11.98	1.60	trace	3.17	..	0.30	...	23
Red hæmatite	69.12	47.47	1.13	trace	trace	trace	0.06	...	5
Spathic ore	49.78	13.98	12.64	1.93	0.22	...	0.11	...	6
Magnetic ore	57.01		0.14		0.10		0.07		1

From this table it will be gathered that, among the most abundant of the iron ores of this country, red hæmatite is the richest and purest,

whilst the brown hæmatite often contains considerable proportions of sulphur and phosphorus, and the spathic ore, though containing little sulphur and phosphorus, often contains much manganese.

The argillaceous ores, or clay iron-stones found in the lias, contain more phosphorus than those from the coal-measures; and these latter, as a general rule, contain more sulphur (pyrites) than the former, although the maximum in the table does not show this.

Clay iron-stone is the ore from which the largest quantity of iron is extracted in England, since it is found abundantly in the coal-measures of Staffordshire, Shropshire and South Wales; and it is a circumstance of great importance in the economy of English iron-smelting that the coal and limestone required in the smelting process, and even the fireclay employed in the construction of the furnace, are found in the immediate vicinity of the ore.

Blackband is the clay iron-stone found in the coalfields of Scotland, and often contains between 20 and 30 per cent. of bituminous matter, which contributes to the economy of fuel in smelting it.

Red hæmatite (Fe_2O_3) is the most characteristic of the ores of iron, occurring in hard, shining, rounded masses, with a peculiar fibrous structure and a dark red-brown colour, whence the ore derives its name (αἷμα, blood). It is found in considerable quantities in Lancashire, Cornwall, the Spanish Peninsula, Algiers, and North America.

Red ochre is a soft variety of this ore, containing a little clay.

Brown hæmatite ($2Fe_2O_3.3H_2O$) is found at Alston Moor (Cumberland) and in Durham, but it is more abundant on the Continent, and is the source of most of the Belgian and French irons. *Pea iron ore* and *yellow ochre* are varieties of brown hæmatite. The Scotch ore, called *kidney-form clay iron-stone*, is really an ore of this class.

The red and brown hæmatites of Lancashire, Cumberland, and Spain are the chief ores used in the manufacture of the variety of pig-iron known as "Bessemer or hæmatite pig."

Specular iron ore (Fe_2O_3) (*oligist ore* or *iron-glance*), although of the same composition as red hæmatite, is very different from it in appearance, having a steel-grey colour and a brilliant metallic lustre. The island of Elba is the chief locality where this ore is found, but it also occurs in Germany, France, and Russia. The excellent quality of the iron smelted from this ore is due partly to the purity of the ore, and partly to the circumstance that charcoal, and not coal, is employed in smelting it.

Magnetic iron ore (Fe_3O_4), of which the *loadstone* is a variety, has a more granular structure and a dark iron-grey colour. It forms mountainous masses in Sweden, and is also found in Russia and North America. It is generally smelted with charcoal and yields an excellent iron. *Iron sand*, a peculiar heavy black sand of metallic lustre, consists in great measure of the magnetic ore, but contains a very large proportion of titanium. It is found abundantly in India, Nova Scotia, and New Zealand; but its fine state of division prevents it from being largely available as a source of iron.

Spathic iron ore ($FeCO_3$) is found in abundance in Saxony, and often contains a considerable quantity of manganese carbonate, which influences the character of the metal extracted from it.

The *oolitic iron ore*, occurring in the Northampton oolite, contains both hydrated sesquioxide and carbonate of iron, together with clay.

Iron pyrites (FeS_2) is remarkable for its yellow colour, its brilliant metallic lustre and crystalline structure, being generally found either in distinct cubical or dodecahedral crystals, or in rounded nodules of radiated structure. It was formerly disregarded as a source of iron, on account of the difficulty of separating the sulphur; but an inferior quality of the metal has been extracted from the residue left after burning the pyrites in the manufacture of oil of vitriol (p. 226), the residue being first well roasted in a lime-kiln to remove as much as possible of the remaining sulphur.

219. *Metallurgy of iron.*—Iron owes the high position which it occupies among useful metals to a combination of valuable qualities not met with in any other metal. Although possessing nearly twice as great *tenacity*

or *strength* as the strongest of the other metals commonly used in the metallic state, it is yet one of the lightest, its specific gravity being only 7·7, and is therefore particularly well adapted for the construction of bridges and large edifices, as well as for ships and carriages. It is the least yielding or malleable of the metals in common use, and can therefore be relied upon for affording a rigid support; and yet its ductility is such that it admits of being rolled into the thinnest sheets and drawn into the finest wire, the strength of which is so great that a wire of $\frac{1}{10}$th inch in diameter is able to sustain 705 pounds, while a similar wire of copper will not support more than 385 pounds.

Being, with the exception of platinum, the least fusible of useful metals, iron is applicable to the construction of fire-grates and furnaces. Nor are its qualifications all dependent upon its physical properties, for it not only enters into a great number of compounds which are of the utmost use in the arts, but its chemical relations to one of the non-metallic elements, carbon, are such, that the addition of a small quantity of this element converts it into *steel*, far surpassing iron in the valuable properties of hardness and elasticity; whilst a larger quantity of carbon gives rise to *cast-iron*, the greater fusibility of which permits it to be moulded into vessels and shapes which could not be produced by forging.

220. *English process of smelting clay iron-stone.*—The first step towards the extraction of the metal consists in calcining (or *roasting*) the ore, in order to expel water and carbonic acid gas. To effect this the ore is sometimes built up, together with a certain amount of small coal, into long pyramidal heaps, resting upon a foundation of large lumps of coal; blackband often contains so much bituminous matter that any other fuel is unnecessary. These heaps are kindled in several places, and allowed to burn slowly until all the fuel is consumed. This calcination has the effect of rendering the ore more porous, and better fitted for the smelting process. If the ore contained much sulphur, a part of it would be expelled by the roasting in the form of sulphurous acid gas. The $FeCO_3$ is converted into Fe_2O_3, which, being a feebler base than FeO, is less likely to combine with silica and form a fusible slag.

More commonly the calcination is effected in kilns resembling lime-kilns, and it is often altogether omitted as a separate process, the expulsion of the water and carbonic acid gas being then effected in the smelting-furnace itself as the ore descends.

The calcined ore is smelted in a huge *blast-furnace A* (Fig. 219) from fifty to eighty feet high, built of massive masonry, and lined internally with firebrick. Since it would be impossible to obtain a sufficiently high temperature with the natural draught of this furnace, air is forced into it at the bottom, under a pressure of three to seven pounds upon the square inch, through *tuyère* or *twyer* pipes *H*, the nozzles *G* of which pass through apertures in three sides of the furnace. As the nitrogen of the air thus forced through the furnace carries away much heat with it, a *hot-blast* is found to economise fuel. To heat the blast the air is passed over firebricks which have been raised to a high temperature by the combustion of the gases which escape from the furnace (see over). In this way the temperature of the blast is frequently raised to 800° C. and that of the furnace when the combustion is most vigorous to 1930° C.

It would be very easy to reduce to the metallic state the oxide of iron contained in the calcined ore, by simply throwing it into this furnace,

together with a proper quantity of coal, coke, or charcoal; but the metallic iron fuses with so great difficulty, that it is impossible to separate it from the clay or *gangue*, as it is called, unless this latter is brought into a liquid state; and even then the fusion of the iron, which is necessary for complete separation, is only effected after it has formed a more easily fusible compound with a small proportion of carbon derived from the fuel.

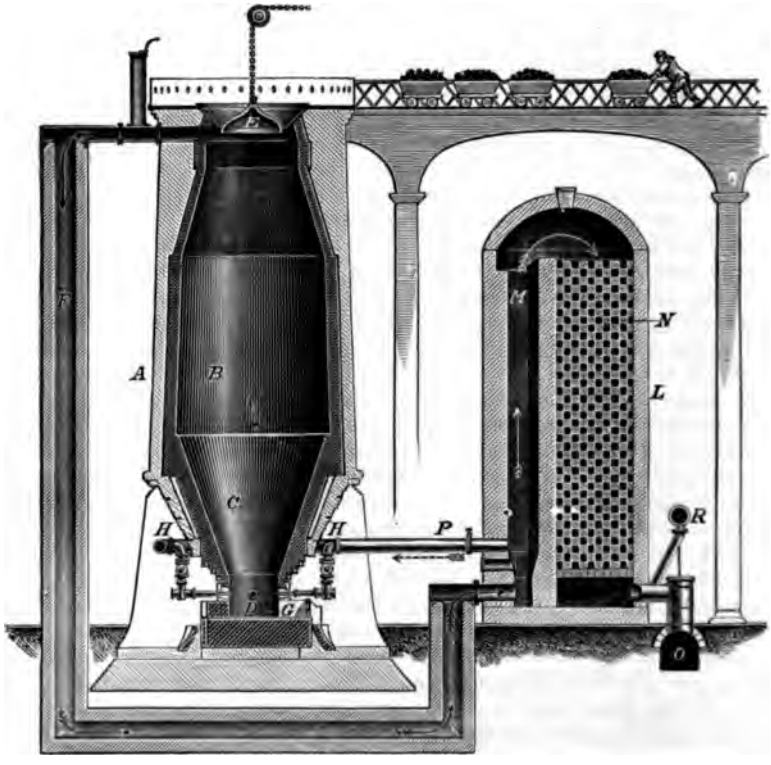


Fig. 219.—Blast-furnace for smelting iron ores.

Now, clay is even more difficult to fuse than iron, so that it is necessary to add, in the smelting of the ore, some substance capable of forming with the clay a combination which is fusible at the temperature of the furnace. If clay (aluminium silicate) be mixed with limestone ($CaCO_3$), and exposed to a high temperature, CO_2 is expelled from the limestone, and the lime unites with the clay, forming a double silicate of alumina and lime, which melts completely, and, when cool, solidifies to a glass or *slag*. The limestone acts as a *flux*, inducing the clay to *flow* in the liquid state. In order, therefore, that the clay may be readily separated from the metallic iron, the calcined ore is mixed with a certain proportion of limestone before being introduced into the furnace.

Great care is necessary in first lighting the blast-furnace lest the new masonry should be cracked by too sudden a rise of temperature, and, when once lighted, the furnace is kept in constant work for years until in want of repair. When the fire has been lighted, the furnace is filled up with coke, and as soon as this has burnt down to some distance below the top opening or *throat*, a layer of the mixture of calcined ore with the requisite proportion of limestone is thrown upon it; over this there is placed another layer of coke, then a second layer of the mixture of ore and flux, and so on, in alternate layers, until the furnace has been filled up; when the layers sink down, fresh quantities of fuel, ore, and flux are added, so that the furnace is kept constantly full. As the air passes from the tuyère pipes into the bottom of the furnace it parts with its oxygen to the carbon of the fuel which it converts into CO_2; the latter, passing over the red-hot fuel in the widest part or *boshes B* of the furnace, becomes CO (see p. 132). It is this carbonic oxide, amounting to some 33 per cent. of the gases, which reduces the calcined ore to the metallic state when it comes in contact with it at that part of the throat of the furnace where the ore has already attained a red-heat. In effecting this reduction, the CO is of course oxidised to CO_2. The metallic iron being infusible at the temperatures at which it is reduced, remains disseminated through the gangue of the ore and as it descends into a hotter region of the furnace some of it reduces CO liberating carbon with which the rest of the iron combines to form cast-iron. At this stage, the clay or gangue of the ore is attacked by the lime which has been produced from the calcination of the limestone flux at a somewhat higher point in the furnace and a fusible *slag* of silicate of lime and alumina is formed. This melts and liberates the disseminated cast-iron at the hottest portion *C* of the furnace, just above the tuyères. The cast-iron now melts and runs together, collecting in the *crucible* or cavity *D* for its reception at the bottom of the furnace. The slag, which has five or six times the bulk of the iron, is allowed to accumulate in the crucible, and to run over its edge down the incline upon which the blast-furnace is built; but when a sufficient quantity of cast-iron has collected at the bottom of the crucible, it is run out through a hole provided for the purpose, either into channels made in a bed of sand, or into iron moulds, where it is cast into rough semi-cylindrical masses called *pigs*, whence cast-iron is also spoken of as *pig-iron*.

A furnace consumes, in the course of twenty-four hours, about 50 tons of coal, 30 tons of ore, 6 tons of limestone, and 100 tons of air. The cast-iron is run off from the crucible once or twice in twelve hours, in quantities of five or six tons at a time. The average yield of calcined clay ironstone is 35 per cent. of iron.

The gases escaping from the blast-furnace are highly inflammable, for they contain as much as 25 per cent. of carbon monoxide;* in modern furnaces the throat is closed when the furnace has been charged, by a bell *E*, and the gases are made to pass through a flue into the *stoves L*, where they are burnt in flues *M* in order to heat the brickwork *N* which is subsequently to raise the temperature of the blast. When one stove has been heated the combustible gases are turned into another stove and an air blast is passed through the first one from pipe *R* in a direction contrary to that of the combustible gases. The pipe *P*

* If coal be used as fuel hydrogen and hydrocarbons will also be present. The gases from a coke-fed furnace contain in 100 vols.: N, 55; CO_2, 18.5; CO, 26.4; H, 0.1 vols.

conducts the blast to the tuyères, and the products of combustion leave the stove by flue *O*. As there is generally more than sufficient combustible gas for this purpose, in some works a portion is burnt in gas engines to supply power for the blowing engines, &c.

When coal is used as fuel it is sometimes profitable to pass the gases through cooling apparatus before they are burnt, in order to condense the tar and ammonia which they contain.

Although the bulk of the nitrogen present in the air escapes unchanged from the furnace, it is not improbable that a portion of it contributes to the formation of the cyanide of potassium (KCN), which is produced in the lower part of the furnace, the potassium being furnished by the ashes of the fuel. Cyanogen is generally found in the escaping gases.

The *slag from the blast-furnace* is essentially a glass composed of a double silicate of aluminium and calcium, the composition of which varies much according to the nature of the earthy matters in the ore and the composition of the flux. Its colour is generally grey, streaked with blue, green, or brown.

The nature of the flux employed must, of course, be modified according to the composition of the *gangue* present in the ore. Where this consists of clay (silicate of alumina), that is, is acid in character, the addition of lime (which is sometimes added in the form of limestone and sometimes as quicklime) will provide for the formation of the double silicate of alumina and lime. But if the iron-ore happened already to contain limestone, a basic gangue, an addition of clay would be necessary, or if quartz were present, consisting of silica only, both lime and alumina (in the form of clay) will be necessary as a flux. It is sometimes found economical to employ a mixture of ores containing different kinds of gangue, so that one may serve as a flux to the other. If a proper proportion of lime were not added, a portion of the oxide of iron would serve as the base to combine with the silica and be carried off in the slag; but if too large a quantity of lime be employed, it will diminish the fusibility of the slag, and prevent the complete separation of the iron from the earthy matter.

The most easily fusible slag which can be formed by the action of lime upon clay has the composition $6CaO.Al_2O_3.9SiO_2$; but in English furnaces, where coal and coke are employed, it is found necessary to use a larger proportion of lime to convert the sulphur of the fuel into calcium sulphide, so that the slag commonly has a composition more nearly represented by the formula $12CaO.2Al_2O_3.9SiO_2$, which would express a compound of 6 molecules of normal calcium silicate with 1 molecule of normal aluminium silicate; $6Ca_2SiO_4.Al_4(SiO_4)_3$.

Since iron, manganese, and magnesium are commonly found occupying the place of a portion of the calcium, a more general formula for the slag from English blast-furnaces would be $6(CaFeMnMg)_2SiO_4.Al_4(SiO_4)_3$.

A fair impression of the ordinary composition of the slag from blast-furnaces is conveyed by the following table:

Slag from Blast-Furnace; in 100 parts.

Silica	43.07	Oxide of manganese (MnO)	1.37
Alumina	14.85	Potash (K_2O)	1.84
Lime	28.92	Sulphide of calcium	1.90
Magnesia	5.87	Phosphoric oxide (P_2O_5)	trace
Oxide of iron (FeO)	2.35		

From 10 to 30 cwt. of slag are produced per ton of cast-iron smelted.

These slags are sometimes run from the blast-furnace into iron moulds, in which they are cast into blocks for rough building purposes. The

presence of a considerable proportion of potash has led to experiments upon their employment as a manure, for which purpose they have been blown out, when liquid, into a finely divided frothy condition fit for grinding and applying to the soil. They are also used for making cement. By blowing air through the slag, it is converted into a substance resembling spun glass, and used, under the name of *slag wool* or *mineral cotton*, for packing round steam-pipes, &c.

220. CAST IRON is, essentially, composed of iron with from 2 to 5 per cent. of carbon, but always contains other substances derived either from the ore or from the fuel employed in smelting it. On taking into consideration the energetic deoxidising action in the blast-furnace, it is not surprising that portions of the various oxygen compounds exposed to it should part with their oxygen, and that the elements thus liberated should find their way into the cast iron. In this way the silica is reduced, and its silicon is found in cast iron in quantity sometimes amounting to 3 or 4 per cent. Hæmatite pig is usually rich in silicon, from the presence of silica in an easily reducible condition in the ore. Sulphur and phosphorus are also generally present in cast iron, but in very much smaller proportion; their presence diminishes its tenacity, and the smelter endeavours to exclude them as far as possible, though a small quantity of phosphorus appears to be rather advantageous for some castings, since it augments the fusibility and fluidity of the cast-iron. The sulphur is chiefly derived from the coal or coke employed in smelting, and for this reason charcoal would be preferable to any other fuel if it could be obtained at a sufficiently cheap rate. The ironworks of some parts of Europe enjoy a great advantage in this respect over those of England. The phosphorus is derived chiefly from the phosphates existing in the ore or in the flux.* The proportion of phosphorus taken up by the cast iron increases with the temperature of the blast-furnace. Manganese, amounting to 1 or 2 per cent., is often met with in cast iron, having been reduced from the oxide of manganese, which is usually found in iron ores; its presence generally enables the iron to hold more carbon and less sulphur. Other metals, such as chromium, cobalt, &c., are also occasionally present, though in such small quantities as to be of no importance in practice.

The following table exhibits the largest and smallest proportion of the various elements determined in the analysis of upwards of a hundred specimens of cast iron:

Composition of Cast Iron.

	Maximum.		Minimum.	
Carbon	4.81	...	1.04	per cent.
Silicon	4.77	...	0.08	,,
Sulphur	1.06	...	...	,,
Phosphorus	1.87	...	trace	,,
Manganese	6.08	...	trace	,,
Iron	...	...	...	,,

In order to understand the difference observed in the several varieties of cast iron, it is necessary to consider the peculiar relations between iron and carbon. Iron fused in contact with carbon is capable of combining with nearly 6 per cent. of that element, to form a white, brilliant,

* It appears to exist in the iron, at least in some cases, as Fe_4P.

and brittle compound, which may be represented pretty nearly as composed of Fe_4C. Under certain circumstances, as this compound of iron and carbon cools, a portion of the carbon separates from the iron, and remains disseminated throughout the mass in the form of minute crystalline particles very much resembling natural graphite. If a broken piece of iron containing these scales be examined, the fracture will be found to exhibit a more or less dark grey colour, due to the presence of the uncombined carbon, and for this reason a cast iron in which a portion of the carbon has thus separated is commonly spoken of as *grey iron*, whilst that in which the whole of the carbon has remained in combination with the metal exhibits a white fracture, and is termed *white iron* or *bright iron*. Intermediate between these is the variety known as *mottled iron*, which has the appearance of a mixture of the grey and white varieties.

The different condition of the carbon in the two varieties of cast iron is rendered apparent when the metal is dissolved in diluted sulphuric or hydrochloric acid, for any carbon which exists in the uncombined state will then be left, whilst that which had been in combination with the iron passes off in the form of peculiar compounds of carbon and hydrogen, which impart the disagreeable odour perceived in the gas evolved when the metal is dissolved in an acid.

The properties of these two varieties of cast iron are widely different, grey iron being so soft that it may be turned in a lathe, whilst the white iron is extremely hard, and of higher specific gravity, 7.5, that of grey iron being 7.1. Again, although white iron fuses at a lower temperature (1100° C.) than grey iron (1200° C.), the latter is far more liquid when fused, and is therefore much better fitted for casting.

Although the presence of uncombined carbon is the chief point which distinguishes grey from white iron, other differences are commonly observed in the composition of the two varieties. The white iron usually contains less silicon than grey iron, but a larger proportion of sulphur.

The difference in the composition of these three varieties of cast iron is shown in the following table:

	Grey.	Mottled.	White.
Iron	92.00	92.75	94.04
Combined carbon . .	0.30	0.75	3.20
Graphitic carbon . .	3.70	2.90	—
Silicon	2.50	1.00	0.64
Sulphur	0.04	0.15	0.20
Phosphorus . . .	1.50	1.60	1.32
Manganese . . .	0.72	0.47	0.60

As might be expected, it is not easy to tell where a cast iron ceases to be grey and begins to be mottled, or where the mottled iron ends and white iron begins. There are, in fact, eight varieties or *grades* of cast iron in commerce, distinguished by the numbers one to eight, of which No. 1 is dark grey and contains the largest proportion of graphite, which diminishes in the succeeding numbers up to No. 8, which is the whitest iron, the intermediate numbers being more or less mottled.

The particular variety of cast iron produced is to some extent under the control of the smelter. A furnace working with siliceous ores and a high percentage of fuel, at a high temperature, yields an iron containing much silicon, and therefore a grey pig, for the presence of silicon determines the separation of carbon as graphite.

When the furnace is working with a minimum of fuel the iron will contain but little silicon, and will consequently retain all its carbon in combination, giving a white pig. But the metal sometimes varies considerably at different levels in the *crucible* of the furnace, so that pigs of different degrees of greyness are obtained at the same tapping. Mottled cast iron surpasses both the other varieties in tenacity, and is therefore preferred where this quality is particularly desirable.

The extra consumption of fuel, of course, renders the grey iron more expensive. When a furnace is worked with a low charge of fuel to produce a white iron, a larger quantity of iron is lost in the slag, sometimes amounting to 5 per cent. of the metal, whilst the average loss in producing grey iron does not exceed 2 per cent. Ores containing a large proportion of manganese are generally found to yield a white iron.

White iron is usually used as *forge-iron* (that is for conversion into malleable iron), whilst grey iron is used as *foundry-iron* (for making castings) and for conversion into steel.

When grey iron is melted, the particles of graphite to which its grey colour is due are dissolved by the liquid iron, and if it be poured into a cold iron mould so as to solidify it as rapidly as possible, the external portion of the casting will present much of the hardness and appearance of white iron, the sudden cooling having prevented the separation of the graphite. This affords the explanation of the process of *chill-casting* by which shot, &c., made of the soft fusible grey iron, are made to acquire, externally, a hardness approaching that of steel. It is a common practice to produce compound castings, that portion of the mould where chilling and consequent hardness is required being made of thick cast iron, and the other part, which is to give a tougher and a softer casting, of sand. When white pig-iron is melted at an extremely high temperature (in a Siemens furnace) and slowly cooled, it becomes grey.

When grey iron is re-melted in the foundry for casting it becomes harder, both because some of the silicon is eliminated by oxidation, causing a corresponding amount of the graphite to pass into combination, and because sulphur is absorbed from the fuel with which the iron is melted.

By the use of ores containing an unusually large proportion of any of the foreign constituents which enter into the reduced iron, the blast-furnace may be made to produce special irons, which have particular applications. Thus, *ferro-silicon* (iron rich in silicon) used for converting white iron into grey iron, *ferro-manganese* (iron containing 68–80 per cent. of Mn; *spiegel-eisen* contains about 10 per cent of Mn), and *ferro-chromium* (containing 60–70 per cent. of Cr) are made; the last two are used in steel-making.

Pig-iron has a very limited application as a building material on account of its low tensile strength (8 tons per sq. in.) and its lack of malleability. For constructional use it must be converted into *malleable* iron which possesses a high tensile strength and is capable of being forged. In order to effect this conversion the silicon, phosphorus and sulphur of the pig-iron must be removed, and the content of carbon must be reduced to below 2 per cent. The attainment of these ends is rendered possible by the fact that the impurities are more readily oxidised than is the iron, and this oxidation may be effected either by mixing the hot iron with iron oxide, or by blowing air through the molten metal. The carbon is thus evolved in the form of CO, whilst the silicon and phosphorus are oxidised to SiO_2 and P_2O_5, both of which oxides are capable of uniting with a base (FeO or CaO) and of being removed as slag.

Before the production and maintenance of very high temperatures was understood, it was customary to heat the iron until it became pasty

and to mix it with iron oxide whilst in this condition (a process known as *puddling*); the impurities, oxidised at the expense of the ferric oxide, were then squeezed out of the iron by working the pasty mass under the hammer. The product was known as *wrought iron*, and, since it was not necessary to *fuse* the iron at any stage of the process, it was possible to reduce the carbon to a very low percentage, for it will be remembered that it is the presence of this element which lowers the fusing-point of iron. At the present day it is possible to keep iron containing very little carbon in a state of fusion, so that the iron oxide can be mixed with it in this condition and the *decarburised* iron can be cast into ingots prior to being rolled into plates or bars (*Siemens-Martin process*). Instead of iron oxide, air is frequently used as the oxidant, in which case it is blown through the molten iron, the heat generated by the oxidation of the impurities serving to keep the metal in fusion (*Bessemer process*). By this method also the metal is obtained in the form of cast ingots.

The original distinction between cast iron, wrought iron and steel lay in their content of carbon. Cast iron contains 3–5 per cent. of C; wrought iron under 0.1 per cent., and steel 0.5–2.0 per cent. The term *ingot iron* is now employed to signify all iron made by methods involving fusion, and includes all grades of refined iron except the very softest and the very hardest (hard steel); the expression *mild steel* is nearly synonymous with ingot iron.

Conversion of cast iron into bar or wrought iron.—Puddling. With pig-iron containing much graphite and silicon, namely grey iron, the puddling process is preceded by the process of *refining*, which will therefore be first described.

Refining cast iron.—This process consists essentially in exposing the metal, in the fused state, to the action of a blast of air in which part of the oxygen has been converted into carbonic oxide by passing over red-hot coke or charcoal.

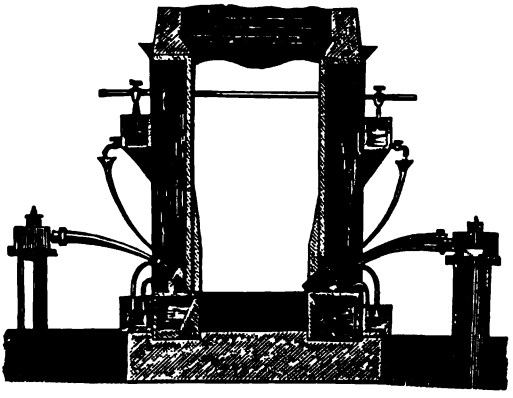


Fig. 220.—Hearth for refining pig-iron.

The *refinery* (Fig. 220) is a rectangular trough with double walls of cast iron, between which cold water is kept circulating to prevent their fusion. This trough is about 3½ feet long by 2½ feet wide, and usually lined with fireclay: on each side of it are arranged three tuyère pipes for the supply of air, inclined at an angle of 25° to 30° to the bottom of the furnace, which is fed with coke, unless the very best iron is required, as for the manufacture of tin-plate, when charcoal is generally used in the refinery.

This furnace having been filled to a certain height with fuel, five or six pigs of iron (from 20 to 30 cwt.) are arranged symmetrically upon it, and covered with coke, a blast of air being forced in through the tuyères, under a pressure of about

3 lbs. upon the square inch. In about a quarter of an hour the metal begins to fuse gradually, and to trickle down through the fuel to the bottom of the refinery, a portion of the iron being converted into oxide in its descent, by the air issuing from the tuyère pipes. When the whole of the metal has been fused, the air is still allowed to play for some time upon its surface, when the fused metal appears to boil in consequence of the escape of bubbles of carbonic oxide.

After about two hours the tap-hole is opened, and the molten metal run out into a flat cast-iron mould kept cold by water, in order to chill the metal and render it brittle. The plate of *refined iron* thus obtained is usually about 2 inches thick. The slag (or *finery cinder*) is generally received in a separate mould; its composition may be generally expressed by the formula $2FeO.SiO_2$, the silica having been derived from the silicon contained in the cast iron.

The change effected in the composition of the iron by the process of refining will be apparent from the following *percentage composition of refined iron:* Fe, 95.14; C, 3.07; Si, 0.63; S, 0.16; P, 0.73; Mn, trace; slag, 0.44. The carbon, therefore, is not nearly so much diminished as the silicon, which is in some cases reduced to $\frac{1}{10}$ of its former proportion by the refining process. The main effect of the refining is to convert the graphite into combined carbon, that is, to make the grey iron white iron; no doubt this conversion is connected with the removal of the silicon; its practical advantage resides in the fact that the white iron passes through a pasty stage before it melts, so that it is better fitted than grey iron for puddling. Half of the sulphur is also sometimes removed by the refining, being found in the slag as sulphide of iron. The phosphorus is not removed to the same extent, though some of it is converted into ferrous phosphate, which may be found in the finery cinder.

It will be seen that the term "refining" is somewhat misapplied to the process of the refinery hearth, as but little of the carbon which must be removed in order to obtain a malleable iron is separated by the operation. The purification proper could not be effected in the refinery, since the fusibility of the iron is so greatly diminished, as it approaches to a pure state, that it could not be kept fluid at the temperature attainable in this furnace, and a more spacious hearth is required upon which the pasty metal may be kneaded into close contact with the oxide of iron which is to complete the oxidation and separation of the carbon. For this reason the metal is transferred to the puddling furnace.

The *puddling* process is carried out in a reverberatory furnace (Figs. 221, 222) connected with a tall chimney provided with a damper, so as to admit of a very perfect regulation of the draught. A bridge of firebrick between the grate and the hearth prevents the contact of the coal with the iron to be puddled. The hearth is composed either of fire-brick or of cast-iron plates, covered with a layer of very infusible slag, and cooled by a free circulation of air between them. This hearth is about 6 feet in length by 4 feet in the widest part near the grate, and 2 feet at the opposite end; it is slightly inclined towards the end farthest from the grate, and finishes in a very considerable slope, at the lowest point of which is the *floss-hole* for the removal of the slag. Since the metal is to attain a very high temperature in this furnace (estimated at 1300°C.), the latter is usually covered with an iron casing, so as to prevent any entrance of cold air through chinks in the brickwork.

About 5 cwt. of the *fine* metal is broken up and heaped upon the hearth of this furnace, together with about 1 cwt. of iron scales (black

oxide of iron, Fe_3O_4), and of *hammer-slag* (basic silicate of iron, obtained in subsequent operations), which are added in order to assist in oxidising the impurities. When the metal has fused, the mass is well stirred or puddled, so that the oxide of iron may be brought into contact with every part of the metal, to effect the oxidation of the impurities. The metal now appears to boil, in consequence of the escape of carbonic oxide, and in about an hour from the commencement of the puddling,

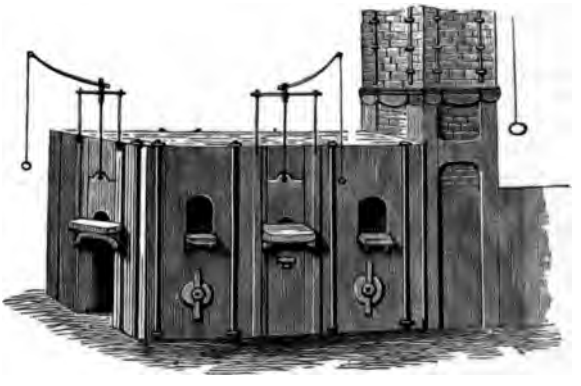


Fig. 221.—Puddling-furnace (elevation).

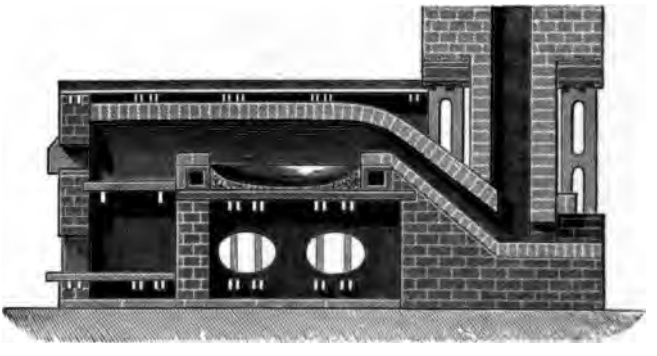


Fig. 222.—Puddling-furnace (section).

so much of the carbon has been removed that the fusibility of the metal is considerably diminished, and instead of retaining a fused condition at the temperature prevailing in the furnace, it assumes a granular *sandy* or *dry* state, spongy masses of pure iron separating or *coming to nature* in the fused mass. The puddling of the iron is continued until the whole has assumed this granular appearance, when the evolution of carbonic oxide ceases almost entirely, showing that the removal of the carbon is nearly completed. The damper is now gradually raised so as to increase the temperature and soften the particles of iron, in order that they may be collected into a mass; and, the more easily to effect this, a part of the slag is run off through the floss-hole. The workman then collects some of the iron upon the end of the paddle, and rolls it

about on the hearth until he has collected a sort of rough ball of iron, weighing about half a hundredweight. When all the iron has been collected into balls in this way, they are placed in the hottest part of the furnace, and pressed occasionally with the paddle, so as to squeeze out a portion of the slag with which their interstices are filled. The doors are then closed to raise the interior of the furnace to a very high temperature, and after a short time, when the balls are sufficiently heated, they are removed from the furnace, and placed under a steam hammer, which squeezes out the liquid slag, and forces the softened particles of iron to cohere into a continuous oblong mass or *bloom*, which is then passed between rollers, by which it is extended into bars. These bars, however (*Rough* or *Puddled*, or *No.* 1 *Bar*), are always hard and brittle, and are not fit for use. In order to improve the tenacity of the iron, the rough bars are cut up into short lengths, which are made into bundles, and, after being raised to a high temperature in the *mill-furnace*, are passed through rollers, which weld the several bars into one compound bar, to be subsequently passed through other rollers until it has acquired the desired dimensions. By thus *fagoting* or *piling* the bars, their texture is rendered far more uniform, and they are made to assume a fibrous structure, which greatly increases their strength (*Merchant Bar*, or *No.* 2 *Bar*). To obtain the best, or *No.* 3 *Bar*, or *wire-iron*, these bars are doubled upon themselves, raised to a welding-heat, and again passed between rollers. These repeated rollings have the effect of thoroughly squeezing out the slag which is mechanically entangled among the particles of iron in the rough bar, and would produce flaws if allowed to remain in the metal. A slight improvement appears also to be effected in the chemical composition of the iron during the rolling, some of the carbon, silicon, phosphorus, and sulphur, still retained by the puddled iron, becoming oxidised, and passing away as gas and slag.

The following table exhibits the change in chemical composition which occurs in pig-iron when puddled (without previous refining) and rolled into wire-iron:

Effect of Puddling and Forging on Cast Iron.

In 100 parts.	Carbon.	Silicon.	Sulphur.	Phosphorus.
Grey pig-iron . .	2.275	2.720	0.301	0.645
Puddled bar. . .	0.296	0.120	0.134	0.139
Wire-iron . . .	0.111	0.088	0.094	0.117

About 90 parts of bar-iron are obtained from 100 of refined iron by the puddling process, the difference representing the carbon which has passed off as carbonic oxide, and the silicon, sulphur, phosphorus, and iron which have been removed in the slag or *tap-cinder*, this being essentially a mixture of ferrous and ferric silicates, varying much in composition according to the character of the iron employed for puddling, and the proportions of iron-scale and hammer-slag introduced into the furnace. Of course, also, the material of which the hearth is composed (the *fettling*) will influence the composition of the slag. The following table affords an illustration of its percentage composition:

Tap-cinder from Puddling-Furnace.

Ferrous oxide (FeO) . .	57.67	Ferrous Sulphide . .	7.07
Ferric oxide (Fe_2O_3) . .	13.53	Lime	4.70
Silica.	8.32	Oxide of manganese .	0.78
Phosphoric oxide (P_2O_5) .	7.29	Magnesia . . .	0.26

The lime in the above cinder was probably derived from the hearth of the furnace, which is sometimes lined with that material to assist in removing the sulphur.

When grey pig-iron is puddled without undergoing the refining process, it becomes much more liquid than white pig or refined iron, and the process is sometimes described as the *pig-boiling process*, whilst refined iron undergoes *dry puddling*. In the latter, the oxygen of the air has more share in the de-carburising of the iron than it has in the former.

Formerly it was sometimes the custom to make a *puddled-steel*, by arresting the puddling process at an earlier stage than usual, so as to leave a proportion of carbon varying from 0.3 to 1 per cent.

It will be observed that this process of puddling is attended with some important disadvantages; it involves a great expenditure of manual labour, and of a most exhausting kind; the wear and tear of the puddling furnace is very considerable, and since it receives only ten or eleven charges of about 5 cwts. each in the course of twenty-four hours, it is necessary to work five or six puddling-furnaces at once, in order to convert into bar-iron the whole of the cast iron turned out from a single blast-furnace. These considerations have led to several attempts to improve the puddling process by employing revolving furnaces and other mechanical arrangements to supersede the heavy manual labour. In *Dankes' rotating puddling-furnace* the pig-iron is run into a cylindrical chamber lined with a mixture of hæmatite and lime. Air is supplied by a fan, and the cylinder is revolved so as to bring the metal thoroughly into contact with the oxides of iron, which form part of the charge, as in the ordinary puddling process. The charge of about 600 lbs. is turned out in a single ball, which is further treated as usual.

Properties of bar-iron.—Even the best bar-iron contains from 0.1 to 0.2 per cent. of carbon, together with minute proportions of silicon, sulphur, and phosphorus. Perfectly pure iron is inferior in hardness and tenacity to that which contains a small proportion of carbon.

Bar-iron is liable to two important defects, which are technically known as *cold-shortness* and *red-shortness*. Cold-short iron is brittle at ordinary temperatures, and appears to owe this to the presence of phosphorus, of which element 0.5 per cent. is sufficient materially to diminish the tenacity of the iron. When the iron is liable to brittleness at a red heat, it is termed red-short iron, and a very little sulphur is sufficient to affect the quality of the iron in this respect.

Not only may the proportions of carbon, silicon, sulphur, phosphorus, and manganese be supposed to affect the quality of the iron, but the state of combination in which these elements exist in the mass is not unlikely to cause a difference. It also appears certain that the mechanical structure, dependent upon the arrangement of the particles composing the mass of metal, has at least as much influence upon the tenacity of the iron as has its chemical composition.

The best bar-iron, if broken slowly, always exhibits a fibrous structure, the particles of iron being arranged in parallel lines. This appears to contribute greatly to the strength of the iron, for when it is wanting, and the bar is composed of a fused mass of crystals, it is weaker in proportion to the size of the crystals. The presence of phosphorus is said to favour the formation of large crystals, and hence to produce cold-shortness. There is some reason to believe that the fibrous is sometimes exchanged for the crystalline texture under the influence of frequent vibrations, as in the case of railway axles, girders of suspension-bridges, &c.

Considering the difficult fusibility of bar-iron, it is fortunate that it possesses the property of being *welded;* that is, of being united by hammering when softened by heat. It is customary first to sprinkle the heated bars with sand or clay in order to convert the superficial oxide of iron into a liquid silicate, which will be forced out from between them by hammering or rolling, leaving the clean metallic surfaces to adhere.

221. *Production of ingot-iron* (*mild steel*).— In the *Siemens-Martin* or *open-hearth* process the pig-iron is melted in a saucer-shaped depression made of iron plates lined with *ganister*, a fairly pure sand; this *hearth* is built in a furnace which is so constructed that a flame of carbon monoxide (producer gas), raised to a very high temperature by the system of regenerative firing (see *Chemistry of Fuel*), plays across the hearth. When the pigs have been thoroughly melted, scraps of iron plate, which, since they are of no other value, may be used to dilute the impure iron, are stirred in, and these are followed by an appropriate quantity of iron oxide, generally hæmatite. The oxidation of the impurities in the iron is effected in part by the oxygen of the hæmatite and in part by the excess of oxygen in the flame used to heat the hearth, the temperature of which is about 1500° C. When the aspect of a test piece withdrawn and hammered by the furnace-man indicates that the process is complete (in 8–10 hours), the tamping-hole of the hearth is unstopped, the metal run into a ladle, and thence into ingot-moulds.

In this process the silicon and phosphorus are removed, chiefly in the form of iron silicate and phosphate, as slag, which floats on the surface of the metal, and in order that the complete removal of the phosphorus may be effected the oxidation must be carried sufficiently far to oxidise nearly the whole of the carbon in the iron, producing a very soft metal. Since for most purposes this product would be too soft, it is customary to bring up the carbon content of the metal in the ladle by the addition of a small quantity of *ferro-manganese*, which immediately melts and mixes with the charge. Ferro-manganese is an alloy of iron and manganese (74 per cent.), the presence of which enables the alloy to hold much carbon (5 per cent.). The yield by this process is about 95 per cent. of the iron charged into the furnace.

In the *Bessemer process* the molten pig-iron is run into a *converter*, which is a large vessel of the shape shown in Fig. 223. It is made of iron plates and is lined with ganister. At the bottom of the vessel there is a number of openings of about ¼-inch in diameter (A) through which air is blown at a pressure of 15 or 20 lbs. to the square inch. The charge (about 10 tons) having been melted in a separate furnace is run into the converter which is suspended on trunnions so that it may be turned into a horizontal position for this purpose, and then erected again into the vertical position. The converter is previously heated by a little burning coke, and the blast is turned on before the iron is charged in so that the liquid iron may not run into the air tubes. The silicon and manganese burn first in the stream of air, producing a very

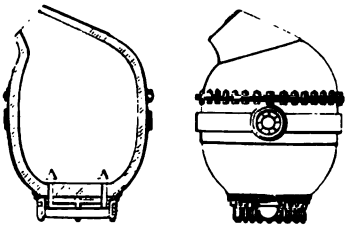


Fig. 223.
Bessemer's converting vessel.

high temperature, then the carbon is converted into carbon monoxide, which burns with a long flame at the mouth of the converter, and a little of the iron is burnt to oxide, which forms a slag with the silica and is carried up as a froth to the surface of the liquid iron. The blast of air, or *blow*, is continued for about twenty minutes, when the disappearance of the flame of CO indicates the completion of the process; but the remaining purified iron is not pasty as in the puddling-furnace, being retained in a perfectly liquid condition by the high temperature (1580° C.) resulting from the combustion of the silicon and manganese, so that the metal may be run out into ingot-moulds by tilting the converter. As in the case of the Siemens-Martin process, the desired hardness is imparted to the metal by the addition of ferro-manganese to the converter just before the iron is poured. The yield is about 85 per cent.

In the original Bessemer process the converter was lined, as described above, with ganister (sand); this rendered the method applicable only to such grades of pig-iron as were fairly free from phosphorus, because the most efficient means of removing this element, namely, the admixture of the strong base lime with the charge, was impossible, on account of the ease with which lime combines with silica, destroying the lining of the furnace. It is now customary to line converters which are to be used for phosphoric pig with a basic material, namely, a mixture of magnesia and lime, made by calcining dolomite. This *basic Bessemer process* is conducted as described above, save that lime to the extent of 15–20 per cent. of the charge of iron is thrown into the converter before the iron is run in. This lime combines with the P_2O_5 produced by the oxidation of the phosphorus, as well as with the silica produced by the oxidation of the silicon. The basic slag formed in this way is useful as a manure, for the sake of its phosphorus (see *Chemistry of Vegetation*). The following percentage compositions illustrate the effect of the two processes :—

	C.	Si.	Mn.	S.	P.
Acid Bessemer pig . . .	3.57	2.26	0.04	0.10	0.07
After blow	0.19	trace	trace	0.10	0.07
After ferro-manganese . .	0.37	trace	0.54	0.09	0.05
Basic Bessemer pig . . .	3.57	1.70	0.71	0.06	1.57
After blow	trace	—	trace	0.05	0.08
After ferro-manganese . .	0.12	0.03	0.27	0.04	0.02

Properties of ingot iron (*mild steel*).—Owing to the fact that bar-iron is not fused whilst ingot iron is completely fused in the process of its manufacture, the main difference between these two forms of iron is that ingot iron does not show the fibrous structure of bar-iron, and is, moreover, free from particles of intermixed slag. Ingot iron is liable to the same defects as bar-iron, and these are due to the same causes.

222. *Manufacture of tool-steel* (*hard steel*).—Steel differs from bar-iron in possessing the property of becoming much harder when heated to redness, and then suddenly cooled by being plunged into water. Perfectly pure iron obtained by the electrotype process is not hardened by sudden cooling; but all bar-iron which contains carbon exhibits this property in a greater or smaller degree according to the proportion of carbon present. It does not become decidedly steely, however, until the

carbon amounts to 0.25 per cent. The term steel was formerly applied only to iron containing enough carbon (not less than 0.75 per cent.) to harden it sufficiently for cutting implements, but all iron containing more than 0.2 per cent. of carbon is now referred to as (*mild*) steel. The hardest steel contains about 1.2 per cent. of carbon, and when the proportion reaches 1.5 per cent. the metal begins to assume the properties of white cast iron. Bar-iron may, therefore, be converted into *hard steel* by the addition of about 1 per cent. of carbon, and, conversely, cast iron is converted into *mild steel* when the quantity of carbon contained in it is reduced to from 0.2 to 0.5 per cent.*

Since the presence of even the small quantities of impurities, other than carbon, which cannot be eliminated by the above processes for making ingot iron are fatal to the best hard steel, this material must be made from the best bar-iron.

The process is known as *cementation*, the bars of iron being imbedded in charcoal and exposed for several days to a high temperature.

The operation is effected in large chests of firebrick or stone, about 10 or 12 feet long by 3 feet wide and 3 feet deep.

Fig. 224.—Furnace for converting bar-iron into steel.

Two of these chests are built into a dome-shaped furnace (*converting-furnace*, Fig. 224), so that the flame may circulate round them, and the furnace is surrounded with a conical jacket of brickwork in order to allow a steady temperature to be maintained in it for some days. The charcoal is ground so as to pass through a sieve of $\frac{1}{4}$-inch mesh, and spread in an even layer upon the bottom of the chests. Upon this the bars of iron, which must be of the best quality, are laid in regular order, a small interval being left between them, which is afterwards filled in with the charcoal powder, with a layer of which the bars are now covered; over this more bars are laid, then another layer of charcoal, and so on until the chest is filled. Each chest holds 5 or 6 tons of bars. One of the bars is allowed to project through an opening in the end of the chest, so that the workmen may withdraw it from time to time and judge of the progress of the operation. The whole is covered in with a layer of about 6 inches of damp clay or sand, or *grinder's waste* (silica and oxide of iron).

* Many metallurgists are of opinion that manganese has an influence similar to that of carbon in converting iron into steel.

The fire is carefully and gradually lighted, lest the chests should be split by too sudden application of heat, and the temperature is eventually raised to about the fusing-point of copper (2000° F., 1090° C.), at which it is maintained for a period varying with the quality of steel which it is desired to obtain. Six or eight days suffice to produce steel of moderate hardness; but the process is continued for three or four days longer if very hard steel be required. The fire is gradually extinguished, so that the chests are about ten days in cooling down.

On opening the chests the bars are found to have suffered a remarkable change both in their external appearance and internal structure. They are covered with large blisters, obviously produced by some gaseous substance raising the softened surface of the metal in its attempt to escape. It is conjectured that the blisters are caused by carbonic oxide produced by the action of the carbon upon particles of slag accidentally present in the bar. On breaking the bars across, the fracture is found to have a finely granular structure, instead of the fibrous appearance exhibited by bar-iron. Chemical analysis shows that the iron has combined with about 1 per cent. of carbon, and the most remarkable part of the result is that this carbon is not only found in the external layer of iron, which has been in direct contact with the heated charcoal, but is also present in the very centre of the bar. It is this transmission of the solid carbon through the solid mass of iron which is implied by the term *cementation*. The chemistry of the process probably consists in the formation of carbonic oxide from the small quantity of atmospheric oxygen in the chest, and the removal of one-half of the carbon from this carbonic oxide, by the iron, which it converts into steel, leaving carbonic acid gas ($2CO - C = CO_2$) to be re-converted into carbonic oxide by taking up more carbon from the charcoal ($CO_2 + C = 2CO$), which it transfers again to the iron. Experiment has shown that soft iron is capable of absorbing mechanically 4.15 volumes of carbonic oxide at a low red heat, so that the action of the gas upon the metal may occur throughout the substance of the bar. The carbonic oxide is retained unaltered by the iron after cooling, unless the bar is raised to the temperature required for the production of steel.

The *blistered steel* obtained by this process is, as would be expected, far from uniform either in composition or in texture; some portions of the bar contain more carbon than others, and the interior contains numerous cavities. In order to improve its quality it is subjected to a process of fagoting similar to that mentioned in the case of bar-iron; the bars of blistered steel, being cut into short lengths, are made up into bundles, which are raised to a welding heat, and placed under a tilt-hammer weighing about 2 cwt., which strikes two or three hundred blows in a minute; in this way the several bars are consolidated into one compound bar, which is then extended under the hammer till of the required dimensions. The bars, before being hammered, are sprinkled with sand, which combines with the oxide of iron upon the surface, and forms a vitreous layer which protects the bar from further oxidation. The steel which has been thus hammered is much denser and more uniform in composition; its tenacity, malleability, and ductility are greatly increased, and it is fitted for the manufacture of shears, files, and other tools. It is commonly known as *shear steel*. Double shear

steel is obtained by breaking the tilted bars in two, and welding these into a compound bar.

The best variety of steel, however, which is perfectly homogeneous in composition, is that known as *cast steel* or *crucible steel*, to obtain which about 50 lbs. of blistered steel are broken into fragments, and fused in a fireclay or plumbago crucible, heated in a wind-furnace, the surface of the metal being protected from oxidation by a little glass melted upon it. The fused steel is cast into ingots, several crucibles being emptied simultaneously into the same mould.

Cast steel is far superior in density and hardness to shear steel, but since it is exceedingly brittle at a red heat, great care is necessary in forging it. It has been found that the addition, to 100 parts of the cast steel, of 1 part of a mixture of charcoal and oxide of manganese, produces a fine-grained steel which admits of being cast on to a bar of wrought iron in the ingot-mould, so that the tenacity of the latter may compensate for the brittleness of the steel when the compound bar is forged, the wrought iron forming the back of the implement, and the steel its cutting edge. Manganese has a stronger attraction than iron has for oxygen and sulphur; hence it would decompose any sulphide or oxide of iron present in the metal, and carry those elements into the slag. The soundness of steel ingots is often impaired by minute bubbles or *blow-holes*, formed by CO or H, the former produced by the action of the carburised iron on a portion of oxidised iron, the latter by the decomposition of moisture in the air. To obviate this, the steel is sometimes subjected to a pressure of several tons on the square inch, while it is solidifying (*Whitworth's steel*).

Some small instruments, such as keys, gun-locks, &c., which are exposed to considerable wear and tear by friction, and require the external hardness of steel without its brittleness, are forged from bar-iron, and converted externally into steel by the process of *case-hardening*, which consists in heating them in contact with some substance containing carbon (such as bone-dust, yellow prussiate of potash, &c.), and afterwards chilling in water. A process which is the reverse of this is adopted in order to increase the tenacity of stirrups, bits, and similar articles made of cast iron; by heating them for some hours in contact with oxide of iron or manganese, their carbon and silicon are removed in the forms of carbonic oxide and silica, and they become converted into *malleable cast iron*. A similar effect is produced by heating in sand, the air between its grains affording the required oxygen.

Properties of steel.—After the steel has been forged into the shape of any implement, it is hardened by being heated to redness, and suddenly chilled in cold water, or oil,* or mercury. It can thus be rendered nearly as hard as diamond, at the same time increasing slightly in volume (sp. gr. of cast-steel 7.93; after hardening, 7.66), and considerably in tensile strength, but diminishing in ductility. If the hardened steel be heated to redness and allowed to cool slowly, it is again converted into soft steel, but by heating it to a temperature short of a red heat, its hardness may be proportionally reduced. This is taken advantage of in annealing the steel or "letting it down" to the proper temper. The very hardest steel is almost as brittle as glass, and totally unfit for any ordinary use; but by heating it to a given temperature and allowing it to cool, its elasticity may be increased to the desired extent, without reducing its hardness below that required for the implement in hand. On heating a steel blade gradually over a flame, it will acquire a light yellow colour when its temperature reaches 430° F., from the formation of a thin film of oxide; as the temperature rises, the thickness of the film increases, and at 470° a decided yellow colour is seen, which assumes a brown shade at 490°, becomes purple at 520°,

* Chilling in oil cools the steel less suddenly, on account of the lower specific heat of oil, and therefore does not render it so hard and brittle. It is often spoken of as *toughening*.

and blue at 550°. At a still higher temperature the film of oxide becomes so thick as to be black and opaque. Steel which has been heated to 430°, and allowed to cool slowly, is said to be *tempered to the yellow*, and is hard enough to take a very fine cutting edge; whilst, if *tempered to the blue*, at 550°, it is too soft to take a very keen edge, but has a very high degree of elasticity. The following table indicates the tempering heats for various implements:

Tempering of Steel.

Temperature, F.	Colour.	Implements thus Tempered.
430° to 450°	Straw-yellow	Razors, lancets.
470°	Yellow.	Penknives.
490°	Brown-yellow	Large shears for cutting metal.
510°	Brown-purple	Clasp-knives.
520°	Purple	Table-knives.
530° to 570°	Blue	Watch-springs, sword-blades.

If a knife-blade be heated to redness its *temper is spoilt*, for it is converted into soft steel. In general the steel implements are ground after being tempered, so that they are not seen of the colours mentioned above, except in the case of watch-springs. A steel blade may be easily distinguished from iron by placing a drop of diluted nitric acid upon it, when a dark stain is produced upon the steel, from the separation of the carbon.

According to modern views the change which occurs in the character of steel during the process of hardening, is primarily due to the existence of two allotropic forms of iron, which are distinguished as α-iron and β-iron, the former being present in soft iron, the latter in hard iron.

When pure iron is allowed to cool slowly from a temperature near its melting-point, it is noticed that at 864° C. the rate at which the iron cools undergoes a change, and that the temperature is four-fold as long a time in falling from 864° C. to 852° C., as it is in falling through an equal number of degrees during the whole of the rest of its cooling. The mean of these temperatures, 858° C., is called the *critical temperature* or *transition-point* of iron. It will be obvious that this delay in cooling can only be due to an evolution of heat by the iron, which must indicate some profound change in the nature of the metal at this temperature. Thus, iron below 858° C. must be different in nature from the metal above this temperature. Iron below 852° C. is said to be in the α-condition (*α-ferrite*), whilst above 864° C. it is in the β-condition (*β-ferrite*).

When the polished surface of a sample of iron or steel is etched with a solution of iodine in potassium iodide or of hydrochloric acid in alcohol and viewed by reflected light through the microscope, it is possible to obtain some idea of the structure of the metal. Examination in this manner of many specimens of different grades has led to the conclusion that there are three distinct forms in which the carbon in iron exists, namely, the compound Fe_3C, called *cementite*, the solid solution of carbon in iron, called *martensite*, and *perlite*, a mixture of cementite and iron in constant proportion. Of these forms martensite is that characteristic of steel which has been hardened by quenching from a temperature of about 1000° C.; the structure of such metal is homogeneous and crystalline, and as the same appearance is to be noted in hardened steels of different carbon content no compound of carbon and iron can well be supposed to exist in this case.

When a steel containing 0.8 per cent. of carbon is slowly cooled, there is an arrest in the temperature at 670° C. similar to that occurring at 858° C. in pure iron.

This arrest corresponds with the transformation of the mass into perlite, showing under the microscope an etched surface different from that of hardened steel, constituting, in fact, unhardened steel. Thus the hardening of steel may be supposed to consist in cooling β-iron, which has carbon dissolved in it, so quickly that the mass remains in this form (martensite) and is not transformed into perlite.

When iron containing more than 0.8 per cent. of carbon is cooled there are two arrests noticed, the one above 670° C. and varying with the percentage of carbon, and the other at 670° C. The first corresponds with the separation of cementite, Fe_3C, from the solution of carbon in iron, until the solution contains 0.8 per cent. of carbon, whereupon perlite separates at 670° C. The etched surface appears as a mass of perlite with flakes of cementite embedded therein.

When less than 0.8 per cent. of carbon is present there are also two arrests in the cooling, the first corresponding with the separation of α-iron while the second is at 670° C., as before, and is due to the separation of perlite. The α-iron is malleable iron.

The following chemical observations, which are much older than the foregoing physical demonstration, fully conform with the theory at present held. If hardened steel be dissolved in dilute HCl or H_2SO_4, nearly the whole of the carbon is evolved as hydrocarbons, but when the temper has been let down, so that the steel is completely softened, the carbon is left, on dissolution of the metal in acid, as a dark powder consisting of a *carbide* of iron, Fe_3C. Steel which has been partially tempered in the manner described above, is found to contain the carbon both in the invisible form, which yields hydrocarbons when the metal is dissolved in acids, and in the form of carbide disseminated as grey scales throughout the mass.

Manganese, nickel, chromium, and tungsten, respectively, in steel appear to make it hard however it is cooled, and are used for making specially hard steel. Manganese steel containing 12 per cent. of that metal is non-magnetic, until it has been heated for some hours at 500–600° C., when it becomes magnetic ; if it then be heated above 800° C. and quickly cooled it again becomes non-magnetic. Steel containing 25 per cent. of nickel is magnetic when heated above 500° C. and cooled slowly.

223. *Direct extraction of wrought iron from the ore.*—Where very rich and pure ores of iron, such as hæmatite and magnetic iron ore, are obtainable, and fuel is abundant, the metal is sometimes extracted without being converted into cast iron. It is probable that the iron of antiquity was extracted in this way, for it is doubtful whether cast iron was known to the ancients, and the slag left from old ironworks does not indicate the use of any flux. For such direct extraction the ore is heated in a crucible with charcoal, the combustion being urged by a blast of air from a tuyère pipe. The spongy mass of bar iron thus obtained is hammered as in the puddling process.

The wrought iron produced by this process always contains a larger proportion of carbon than puddled iron, and is therefore somewhat steely in character. In India the native smelters produce iron or steel at will by this process.

Fig. 225.—Fletcher's injector furnace.

224. *Extraction of iron on the small scale.*—In the laboratory, iron may be extracted from hæmatite in the following manner : A fireclay crucible, about 3 inches high, is filled with charcoal powder, rammed down in successive layers ; a smooth conical cavity is scooped in the charcoal, and a mixture of 8 grams red hæmatite, 2 grams chalk, and 2 grams pipeclay, is introduced into it ; the mixture is covered with a layer of charcoal, and a lid placed on the crucible, which is heated in a Fletcher's furnace (Fig. 225) for about half an hour. On breaking the cold crucible a button of cast iron will be obtained.

Nearly pure iron may be prepared by fusing the best wire-iron with about one-fifth of its weight of pure ferric oxide, to oxidise the carbon and silicon which it contains. Some powdered green glass, perfectly free from lead, must be employed as a flux, and the crucible (with its cover well cemented on with fireclay) exposed for an hour to a very high temperature. A silvery button of iron will then be obtained.

225. *Chemical properties of iron.*—Pure iron is prepared by electrolysis. Its sp. gr. is 7.9 and it melts at 1600° C. In its ordinary condition iron is unaffected by perfectly dry air, but in the presence of moisture and carbonic acid gas it is gradually converted into hydrated ferric oxide ($2Fe_2O_3.3H_2O$) or *rust.** The water is decomposed, and ferrous carbonate formed ($Fe + H_2O + CO_2 = FeCO_3 + H_2$); this is dissolved by the carbonic acid present, and the solution rapidly absorbs oxygen from the air, depositing the ferric oxide in a hydrated state; $2FeCO_3 + O = Fe_2O_3 + 2CO_2$. When iron nails are driven into a new oaken fence, a black streak will soon be observed descending from each nail, caused by the formation of tannate of iron (ink) by the action of the tannic acid in the wood upon the solution of carbonate of iron formed from the nails. The diffusion of *iron-mould* stains through the fibre of wet linen by contact with a nail, is also caused by the formation of solution of carbonate of iron. The iron in *chalybeate* waters is also generally present in the form of carbonate dissolved in carbonic acid, and hence the rusty deposit which is formed when they are exposed to the air. Iron does not rust in water containing a free alkali, or alkaline earth, or an alkaline carbonate.

Concentrated H_2SO_4 and HNO_3 do not act upon iron at the ordinary temperature, though they dissolve it rapidly when diluted. Even when boiling, strong sulphuric acid acts upon it but slowly. When iron has been immersed in strong nitric acid (sp. gr. 1.45), it is found to be unattacked† when subsequently placed in HNO_3 of sp. gr. 1.35, unless previously wiped; it is then said to have assumed the *passive state.* If iron wire be placed in HNO_3 of sp. gr. 1.35, it is attacked immediately; but if a piece of gold or platinum be made to touch it beneath the acid, the iron assumes the passive state, and the action ceases at once. A state similar to this, the cause of which has not yet been satisfactorily explained, is sometimes assumed by the other metals, though in a less marked degree. In the case of iron it has been attributed to the formation of a coating of the magnetic oxide, which is sparingly soluble in strong HNO_3.

Ferrum redactum is iron in powder obtained by reducing Fe_2O_3 with hydrogen at a red heat in an iron tube. It always contains some Fe_3O_4.

226. **Oxides of iron.**—Three compounds of iron with oxygen are known in the separate state; FeO, Fe_3O_4, Fe_2O_3.

Ferrous oxide, or *protoxide of iron*, FeO, is obtained by heating ferric oxide to 500° C. in dry hydrogen; $Fe_2O_3 + H_2 = H_2O + 2FeO$. It is obtained as a grey powder, which readily absorbs O from the air, taking fire and becoming Fe_3O_4. It is a basic oxide, yielding ferrous salts. In the finely divided state it decomposes water.

Ferrous hydroxide, $Fe(OH)_2$, is precipitated by alkalies from the ferrous salts. When pure it forms a white precipitate, but if air be present it becomes green from

* Most samples of rust are magnetic, indicating the presence of the magnetic oxide.

† It is doubtful whether the iron ever remains quite unattacked, although no gas is evolved.

the production of ferroso-ferric oxide, and ultimately brown ferric hydroxide. These changes are best seen when potash or ammonia is added to the ferrous salt obtained by shaking iron turnings or filings with a strong solution of sulphurous acid. This disposition of the ferrous hydroxide to absorb oxygen is turned to advantage when a mixture of ferrous sulphate with lime or potash is employed for converting blue into white indigo.

Ferric oxide, or *peroxide of iron*, Fe_2O_3, occurs as *specular iron ore* in six-sided crystals, and in hæmatite, as already noticed among the ores of iron, and has also been referred to as occurring in commerce under the names of *colcothar*, *jeweller's rouge*, and *Venetian red*, which are obtained by the calcination of the green sulphate of iron; $2FeSO_4 = Fe_2O_3 + SO_2 + SO_3$. The *ferric hydroxide* obtained by decomposing a solution of ferric chloride with an alkali, forms a brown gelatinous precipitate, which is easily dissolved by acids. When freshly precipitated and well washed it dissolves in a solution of ferric chloride, forming a basic chloride which by dialysis is slowly decomposed, HCl passing through the dialyser and a blood-red colloidal solution of $Fe(OH)_3$ being left in the dialyser. When dried at 100° C., the hydroxide becomes $2Fe_2O_3.H_2O$. If a hot solution of a ferric salt be precipitated by an alkali, and the precipitate dried over sulphuric acid, it becomes $Fe_3(OH)_6.Fe_2O_3$, which is the composition of iron-rust and of some brown hæmatites. When either of the hydroxides is heated to dull redness, it exhibits a sudden glow, and is converted into a modification of Fe_2O_3, which is dissolved with great difficulty by acids, although it has the same composition as the soluble form which has not been strongly heated. When the ferric oxide is heated to whiteness, it loses oxygen, and is converted into magnetic oxide of iron; $3Fe_2O_3 = 2Fe_3O_4 + O$. Existing as it does in all soils, ferric oxide is believed to fulfil the purpose of oxidising the organic matter in the soil, and converting its carbon into carbon dioxide, to be absorbed by the plant: the ferric oxide being thus reduced to ferrous oxide, which is oxidised by the air, and fitted to perform again the same office. Ferric oxide, like alumina, is a weak base, and even exhibits some tendency to play the part of an acid towards strong bases, though not in so marked a degree as alumina. When heated in a stream of H or CO, it yields Fe_3O_4 at 350° C., pyrophoric FeO at 500° C., and metallic iron at from 700° to 800° C.

Magnetic or *black oxide of iron*, or *magnetite*, Fe_3O_4, is generally regarded as a compound of ferrous oxide with ferric oxide ($FeO.Fe_2O_3$), a view which is confirmed by the occurrence of a number of minerals having the same crystalline form as the native magnetic oxide of iron, in which the iron, or part of it, is displaced by other metals. Thus, *spinelle* is $MgO.Al_2O_3$; *Franklinite*, $ZnO.Fe_2O_3$; *chrome-iron ore*, $FeO.Cr_2O_3$; *pleonaste*, $MgO.Fe_2O_3$; *Gahnite*, $ZnO.Al_2O_3$. The natural magnetic oxide was mentioned among the ores of iron, and this oxide has been seen to be the result of the action of air or steam upon iron at a high temperature. The hydrated magnetic oxide of iron ($Fe_3O_4.H_2O$) is obtained as a black crystalline powder by mixing 1 molecule of ferrous sulphate with 1 molecule of ferric sulphate, and pouring the mixture into a slight excess of solution of ammonia, which is afterwards boiled with it. Magnetic oxide of iron, when acted upon by acids, yields mixtures of ferrous and ferric salts, so that it is not an independent basic oxide.

The very stable character of Fe_3O_4 has led to its application for

protecting iron from rust. When superheated steam is passed over the red-hot metal, a very dense strongly adherent film of Fe_3O_4 is produced, which effectually protects the metal (*Barff's process*). A similar coating is produced by the action of a mixture of air and carbonic acid gas (*Bower's process*).

Ferric acid, H_2FeO_4, has not been obtained in the free state, but some of its salts are known.*

When iron filings are strongly heated with nitre, and the mass treated with a little water, a fine purple solution of potassium ferrate is obtained. A better method of preparing this salt consists in suspending 1 part of freshly precipitated ferric hydrate in 50 parts of water, adding 30 parts of solid potassium hydrate and passing chlorine till a slight effervescence commences: $Fe_2O_3 + Cl_6 + 10KOH = 6KCl + 2(K_2FeO_4) + 5H_2O$; the ferrate forms a black precipitate, being insoluble in the strongly alkaline solution, though it dissolves in pure water to form a purple solution, which is decomposed even by dilution, oxygen escaping, and hydrated ferric oxide being precipitated. A similar decomposition happens on boiling a strong solution, or on adding an acid with a view to liberate the ferric acid. The ferrates of barium, strontium, and calcium are obtained as fine red precipitates when solutions of their salts are mixed with potassium ferrate.

As a lecture experiment, the ferrate is readily prepared by dissolving a fragment of KOH in a little solution of Fe_2Cl_6, adding a few drops of bromine, and gently heating. On dissolving the cold mass in water, a fine red solution is obtained, which gives a red granular precipitate with $BaCl_2$.

The pink solution obtained by boiling some samples of chloride of lime with water contains calcium ferrate, and gives a pink precipitate with $BaCl_2$. By boiling Fe_2Cl_6 with excess of chloride of lime, a fine pink solution of calcium ferrate is obtained.

Ferrous carbonate, $FeCO_3$, or *spathic iron ore*, or *siderite*, is found in rhombohedral crystals associated with the carbonates of Ca, Mg, and Mn, which are isomorphous with it. It occurs in chalybeate waters, dissolved in carbonic acid, and deposits as ferric hydrate when the water is exposed to air. If powdered iron which has been reduced from the oxide by hydrogen (*ferrum redactum*) be suspended in water, and a stream of CO_2 be passed for some time, a solution of $FeCO_3$ in carbonic acid is obtained, which, when filtered, is colourless, becomes rusty when exposed to air, and gives, when boiled, an abundant precipitate of $FeCO_3$, which is nearly white, and becomes green when exposed to air. Sodium carbonate added to a ferrous salt gives a white precipitate if all air be excluded; otherwise oxygen is absorbed, and a dingy green precipitate containing Fe_3O_4 is formed.

The substance sold as *ferric carbonate*, obtained by precipitating a ferric salt with sodium carbonate, is mainly ferric hydrate, since weak bases like Fe_2O_3 do not form carbonates.

227. **Ferrous sulphate**, *copperas*, *green vitriol*, or *sulphate of iron*, is easily obtained by heating 1 part of iron wire with 1½ part of strong sulphuric acid, mixed with 4 times its weight of water, until the whole of the metal is dissolved, when the solution is allowed to crystallise. Its manufacture on the large scale by the oxidation of iron pyrites has been already referred to. It forms fine green monoclinic crystals, having the composition $FeSO_4.H_2O.6Aq$. Rhombic crystals, isomorphous with the sulphates Zn and Mg, can also be obtained.

The colour of the crystals varies somewhat, from the occasional presence of small quantities of ferric sulphate, $Fe_2(SO_4)_3$. It dissolves very easily in twice its weight of cold water, yielding a pale green solution. One part of boiling water dissolves about 3 parts of the crystals. When the commercial sulphate of iron is boiled with water it yields a brown

* The common ferrates correspond with an anhydride, FeO_3. Lately a *barium perferrate* corresponding with FeO_4 has been prepared, a fact important from the point of view of the periodic law (p. 302).

muddy solution, in consequence of the decomposition of the ferric sulphate contained in it, with precipitation of a basic sulphate. Ferrous sulphate has a great tendency to absorb oxygen, and to become converted into ferric sulphate, and is thus useful as a reducing-agent. For example, it is employed for precipitating gold in the metallic state from its solutions. But its chief use is for the manufacture of ink and black dyes by its action upon vegetable infusions containing tannic acid, such as that of nut-galls.

Crystals of $FeSO_4.H_2O.4Aq$, isomorphous with $CuSO_4.H_2O.4Aq$, may be obtained by dropping a crystal of cupric sulphate into a supersaturated solution of ferrous sulphate. As in the case of $MgSO_4.7H_2O$ (p. 375) one molecule of the H_2O in $FeSO_4.7H_2O$ may be exchanged for other sulphates; thus, *ammonium ferrous sulphate*, $FeSO_4.(NH_4)_2SO_4.6H_2O$, is well known.

The salt $FeSO_4.SO_3$ is obtained in minute prismatic crystals when a saturated solution of ferrous sulphate is added to an excess of strong sulphuric acid.

Ferric sulphate, $Fe_2(SO_4)_3$, is found in Chili as a white silky crystalline mineral, *coquimbite*, having the composition $Fe_2(SO_4)_3.9Aq$. *Iron alums*, constructed on the type of the common alums (p. 387), with Fe‴ in place of Al‴ (*e.g.*, $NH_4.Fe'''(SO_4)_2.12H_2O$), are commercial salts.

Ferrous phosphate, $Fe_3(PO_4)_2$, and *arsenate*, $Fe_3(AsO_4)_2$, are used in medicine, being prepared by precipitating ferrous sulphate with a mixture of sodium acetate and sodium phosphate or arsenate. The acetate is used so that the resulting liquid may contain free acetic acid instead of the free sulphuric formed by the H in the sodium salt; $3FeSO_4 + 2Na_2HPO_4 = Fe_3(PO_4)_2 + 2Na_2SO_4 + H_2SO_4$. Both the phosphate and arsenate are white when perfectly pure, but they become blue when exposed to air, from the production of a little ferroso-ferric salt. The precipitated *ferric phosphate* is $2FePO_4.5Aq$. Ferrous phosphate is found in the mineral *Vivianite* or *native Prussian blue*, $Fe_3(PO_4)_2.8Aq$.

Ferrous silicate, Fe_2SiO_4, is found crystallised in *finery cinder* of the ironworks.

Ferrous chloride, $FeCl_2$, sublimes in colourless six-sided scales when iron is heated in HCl gas. It is deliquescent, and crystallises from water in pale green crystals, $FeCl_2.4Aq$, which are oxidised by air.

Ferrous iodide, FeI_2, is prepared by digesting fine iron wire with twice its weight of iodine and about eight parts of water for some time, afterwards boiling till the red colour has disappeared, filtering, and evaporating in contact with clean iron. It forms green crystals, $FeI_2.5Aq$, which are deliquescent and very soluble in water. The solution absorbs oxygen from the air, and deposits a brown precipitate unless kept in contact with clean iron or mixed with strong syrup.

228. **Ferric chloride**, or *perchloride of iron* ($FeCl_3$), is obtained in beautiful dark green crystalline scales when iron wire is heated in a glass tube through which a current of dry chlorine is passed, the ferric chloride passing off in vapour, and condensing in the cool part of the tube. The crystals almost instantly become wet when exposed to air on account of their great attraction for water. Ferric chloride may be obtained in solution by dissolving iron in hydrochloric acid, and converting the ferrous chloride ($FeCl_2$) thus formed into ferric chloride by the action of nitric and hydrochloric acids (p. 191). A strong solution yields crystals of $FeCl_3.6Aq$. The aqueous solution reddens litmus. The crystals are decomposed by heat, leaving an oxychloride. The solution of ferric chloride has been recommended in some cases as a disinfectant, being easily reduced to ferrous chloride, and thus affording chlorine to oxidise unstable organic matters (p. 175). In contact with paper, $FeCl_3$ becomes reduced to $FeCl_2$ when exposed to light. A solution of perchloride of iron in alcohol is used in medicine under the name of *tincture of iron*. It is also soluble in ether and benzene.

Solution of ferric chloride dissolves a very large quantity of *pure* freshly precipitated ferric oxide (p. 417), nine molecules of Fe_2O_3 being dissolved by one molecule

of ferric chloride. The solution of ferric *oxychloride* thus obtained has a very dark-red colour, and yields a very copious brown precipitate with common water, or any solution containing even a trace of a sulphate. When the aqueous solution of $FeCl_3$ is heated, it dissociates into a similar soluble hydroxide and HCl.

Ferrous sulphide, FeS, is formed when a red-hot bar of iron is rubbed with a stick of sulphur, the fused FeS running off in globules, and is prepared as described at p. 214. It is obtained as a black precipitate when an alkaline sulphide is added to a ferrous salt. It is easily oxidised when exposed to air in a moist state, and dissolves readily in HCl, being indeed the only black sulphide which dissolves easily in dilute HCl. It is used in the laboratory for making H_2S.

Magnetic pyrites, Fe_7S_8, is found in yellow six-sided crystals.

Iron pyrites, or *mundic,* FeS_2, forms yellow cubes or octahedra of sp. gr. 5.2. It is formed by the slow reduction of ferrous sulphate by organic matter, and its presence in coal appears to be accounted for in this way. Minute crystals of iron pyrites are sometimes found as rough casts of organic substances. It burns when heated, yielding Fe_2O_3 and SO_2, and is largely used as a source of the latter by the vitriol manufacturer. Sulphur itself may be obtained from it by distillation at a high temperature, Fe_3S_4 being left. FeS_2 is insoluble in HCl, which distinguishes it from FeS. It may be dissolved by nitric acid. *Radiated pyrites,* or white pyrites, or *marcasite,* has the same composition, but its sp. gr. is only 4.8.

Some kinds of pyrites explode with considerable violence when heated, and create much alarm when they occur in household coal; these have been found to contain small cavities filled with highly compressed (probably liquid) CO_2, which expands suddenly when heated.

Compact yellow iron pyrites is not oxidised by exposure to air, but white pyrites is easily converted into ferrous sulphate and sulphuric acid. Even yellow, pyrites in minute crystals diffused through clay will behave in the same way.

The FeS_2 may be obtained artificially by heating iron with excess of sulphur to a temperature below redness, or by heating ferric oxide or hydrate moderately in a stream of H_2S as long as it increases in weight.

Iron nitride, a compound of iron with about 9 per cent. of nitrogen, has been found as a silvery deposit on the lavas of Etna. It yields ammonia when heated in hydrogen.

Iron carbonyls.—When finely divided iron, prepared by igniting ferrous oxalate and reducing the resulting oxide in a current of hydrogen, is allowed to remain in the cold in contact with CO, a compound $Fe(CO)_5$, *iron pentacarbonyl,* is formed and can be distilled from the unaltered iron at 120° C. and condensed in a receiver surrounded by ice and salt. It is an amber-coloured liquid of sp. gr. 1.46; it boils at 103° C. and crystallises below − 21° C.; at 180° C. it is decomposed into Fe and CO. It dissolves in many organic solvents, and is slowly decomposed with precipitation of $Fe_2(OH)_6$ on exposure to air. When exposed to sunlight it deposits golden scales which appear to have the composition $Fe(CO)_7$, *iron heptacarbonyl.* The properties of these compounds should be compared with those of nickel carbonyl (p. 425). Iron carbonyl has been detected in coal gas which has been compressed in iron cylinders.

229. *Atomic weight of iron.*—When iron is dissolved in hydrochloric acid, 28 parts by weight of iron combine with 35.5 parts of chlorine, displacing 1 part of hydrogen. The specific heat of iron, and its isomorphism with magnesium, zinc, and cadmium, show that its atomic weight must be represented by 56, so that iron is a diad or divalent element, one atom of iron being exchangeable for two atoms of hydrogen.

The molecular formula of ferric chloride has been confirmed by the determination of the vapour density at 400° C., which has been found to be 165, corresponding with the formula Fe_2Cl_6. But at higher temperatures the vapour density approaches 81.25, corresponding with the formula $FeCl_3$, although it does not quite reach this value, since a certain amount of dissociation into $FeCl_2$ and Cl_2 occurs.

It will be remarked that iron possesses a different valency accordingly

as it exists in ferrous or ferric compounds. Thus, in ferrous oxide (FeO) and ferrous chloride ($FeCl_2$) it occupies the place of two atoms of hydrogen, and is divalent; but in ferric oxide (Fe_2O_3) and ferric chloride ($FeCl_3$) each atom of iron occupies the place of three atoms of hydrogen, and is trivalent.

Iron is remarkable for its two series of fairly stable salts, the ferrous and ferric, the former acting as reducing-agents, and the latter as oxidising agents. Ferrous iron resembles magnesium and zinc in its disposition to form double salts with salts of ammonium, hence its solutions are imperfectly precipitated by ammonia; but ferric iron resembles aluminium, and is completely precipitated. Nitric acid, chloric acid, and chlorine will always convert ferrous into ferric salts, and ensure complete precipitation by ammonia.

Some chemists designate the divalent iron existing in ferrous compounds by the name *ferrosum* (Fe″), and the trivalent iron of the ferric compounds by *ferricum* (Fe‴). Others regard iron as a tetravalent metal Fe^{iv}, existing in the ferrous salts as a group of two atoms united by two bonds, and in the ferric salts as a group of two atoms united by one bond. On this view, ferrous chloride would be Fe_2Cl_4, or $Cl_2{=}Fe{=}Fe{=}Cl_2$, and ferric chloride would be Fe_2Cl_6, or $Cl_3{\equiv}Fe{-}Fe{\equiv}Cl_3$.

COBALT.

Co″ = 58.5 parts by weight.

230. Some of the compounds of cobalt are of considerable importance in the arts, on account of their brilliant and permanent colours. It is generally found in combination with arsenic and sulphur, forming *tin-white cobalt*, $CoAs_2$, and *cobalt glance*, $CoAs_2.CoS_2$, but its ores also generally contain nickel, copper, iron, manganese, and bismuth.

The metal itself is obtained by strongly heating cobalt oxide with charcoal, in the manner to be described for preparing nickel from its oxide, or by heating the oxide with aluminium powder (p. 386). In its properties it closely resembles iron, but it is said to surpass iron in tenacity. It is magnetic. It is heavier than iron, sp. gr. 8.5, and rather more easily fusible (1500° C.). It has been substituted for nickel in plating goods which are usually nickel-plated.

Three oxides of cobalt, corresponding with those of iron, are known: *cobaltous oxide*, CoO; *cobaltic oxide*, Co_2O_3; and *cobalto-cobaltic oxide*, Co_3O_4 or $CoO.Co_2O_3$. The first of these, CoO, is a brown powder left when $Co(OH)_2$ is ignited in absence of air; it is a basic oxide, dissolving in acids to form cobaltous salts. When heated in air, it oxidises to $CoO.Co_2O_3$. When heated in the electric furnace, it melts and forms rose-coloured crystals.

Cobaltic oxide is left as a black powder when cobaltous nitrate is gently heated. It is a feeble base, and the cobaltic salts are very unstable; thus the oxide dissolves in cold HCl, yielding a brown solution of *cobaltic chloride*, Co_2Cl_6, which is easily decomposed when heated, evolving Cl_2 and leaving $2CoCl_2$. When Co_2O_3 is heated it becomes $CoO.Co_2O_3$. It is doubtful whether a cobalt dioxide, CoO_2, exists, but when Co_2O_3 is fused with MgO in the electric furnace, red crystals of $MgCoO_3$ are obtained.

Cobalto-cobaltic oxide is the commercial oxide of cobalt employed for painting on porcelain, and for preparing other commercial cobalt

products. It is a black powder, which evolves chlorine when boiled with HCl, yielding a solution of $CoCl_2$. It is generally prepared as a by-product in the manufacture of nickel from its arsenical ores (see *Nickel*). Co_3O_4 is not an independent base, but gives cobaltous and cobaltic salts when dissolved in acids.

Cobaltous hydroxide, $Co(OH)_2$, is obtained by adding potash in excess to a solution of a cobaltous salt, and boiling. The blue precipitate produced at first is a basic salt which becomes converted into the red hydroxide on boiling with excess of potash. If air be allowed access it oxidises the red precipitate, converting it into brown cobaltic hydroxide. $Co(OH)_2$ dissolves in ammonia, giving a fine red solution, which absorbs oxygen from the air and becomes brown. *Cobaltic hydroxide*, $Co_2(OH)_6$, forms the black precipitate when the solution of a hypochlorite or hypobromite is added to one of a cobaltous salt.

Cobaltous nitrate, $Co(NO_3)_2.6Aq$, obtained by dissolving cobalt oxide in HNO_3 and crystallising, forms red prisms, which become blue when their water is expelled, and black Co_2O_3 on further heating.

Cobalt-yellow or *potassium-cobaltic nitrite*, $K_6CO'''_2(NO_2)_{12}$, is obtained as a yellow precipitate when cobaltous nitrate is acidified with acetic acid, and potassium nitrite added; the acetic acid liberates nitrous acid, which oxidises the cobaltous salt; $2Co''(NO_3)_2 + 10KNO_2 + 4HNO_2 = K_6Co'''_2(NO_2)_{12} + 4KNO_3 + 2NO + 2H_2O$. It forms a yellow crystalline precipitate, slighly soluble in water, and not decomposed by cold HCl or HNO_3. Caustic alkalies decompose it, separating $Co_2(OH)_6$.

Cobaltous chloride ($CoCl_2$), obtained by dissolving any of the oxides in hydrochloric acid, forms red prisms, $CoCl_2.6Aq$, which become blue $CoCl_2.2Aq$ at 120° C., and at 140° C., $CoCl_2$, which may be sublimed in dark blue scales in a current of chlorine. If strong hydrochloric acid be added to a red solution of this salt, it becomes blue; if enough water be now added to render it pink, the blue colour may be produced at pleasure by boiling, the solution first passing through a neutral tint.* Chloride (*muriate*) of cobalt is employed as a *sympathetic ink*, for characters written with its pink solution are nearly invisible until they are held before the fire, when they become blue and resume their original pink colour if exposed to the air; a little chloride of iron causes a green colour.

The *cobaltous sulphide* (CoS) is obtained as a black precipitate when an alkaline sulphide is added to a solution of a salt of cobalt. It differs from FeS by being insoluble in HCl. A *cobaltic sulphide* (Co_2S_3) is found in grey octahedra, forming *cobalt pyrites*. The *disulphide* (CoS_2) has been obtained artificially.

Cobaltous sulphate, $CoSO_4.7H_2O$, is found as *cobalt vitriol*. It forms red prisms isomorphous with ferrous sulphate. It does not become blue when dried, and bears a high temperature without decomposing. *Cobaltic sulphate* and cobaltic alums have been prepared.

Cobaltous arsenate, or *cobalt bloom*, $Co_3(AsO_4)_2.8Aq$, is found in pink needles.

Cobalt di-arsenide, $CoAs_2$ is found crystallised as *tin-white cobalt* and *speiss cobalt*, in which it is associated with the isomorphous arsenides of nickel and iron, so that it is written $[CoNiFe]As_2$. $CoAs_2$ is also found in nature.

The **cobaltous silicate** associated with potassium silicate forms the blue colour known as *smalt*, which is prepared by roasting the cobalt ore, so as to convert the bulk of the cobalt into oxide, leaving, however, a

* A solution containing so small a quantity as 0.015 per cent. of cobalt will give a distinct blue colour when boiled with an equal bulk of strong hydrochloric acid.

considerable quantity of arsenic and sulphur still in the ore. The residue is then fused in a crucible with ground quartz and carbonate of potash, when a blue glass is formed, containing cobalt silicate and potassium silicate; whilst the iron, nickel, and copper, combined with arsenic and sulphur, collect at the bottom of the crucible and form a fused mass of metallic appearance known as *speiss*, which is employed as a source of nickel. The blue glass is poured into cold water, so that it may be more easily reduced to the fine powder in which the smalt is sold. If the cobalt ore destined for smalt be over-roasted, so as to convert the iron into oxide, this will pass into the smalt as a silicate, injuring its colour. Smalt much resembles ultramarine, but is not bleached by acids. *Zaffre* is prepared by roasting a mixture of cobalt ore with two or three parts of sand.

Thénard's blue, or *cobalt ultramarine*, consists of cobalt phosphate and aluminium phosphate, and is prepared by mixing precipitated alumina with cobalt phosphate and calcining in a covered crucible. The phosphate is obtained by precipitating a solution of cobalt nitrate with phosphate of potassium or sodium.

Rinmann's green is prepared by calcining the precipitate produced by sodium carbonate in a mixture of cobalt sulphate with zinc sulphate. It is a compound of the oxides of cobalt and zinc.

The *relations of ammonia to the cobalt salts* are very remarkable and characteristic, the NH_3 combining both with cobaltous and cobaltic salts to form compounds which behave like salts of new bases containing cobalt, nitrogen, and hydrogen, known as *cobaltosamines* and *cobaltamines*.

When NH_3 is added to the solution of a cobaltous salt, air being excluded, a *cobaltosamine* salt of the general type $CoX_2.6NH_3$, where X is an acid radicle, is formed. When these are exposed to the air they undergo oxidation, yielding *oxycobaltamine* salts of the type $CoOX_2.5NH_3$, in which the cobalt may be regarded as tetrad, corresponding with the oxide CoO_2; these salts lose oxygen, becoming cobaltamine salts, when their solutions are heated. If the cobaltosamine solution be fairly dilute when it is exposed to the air, the oxy-salt will not be formed, and on addition of an acid a *cobaltamine* salt will be separated. These are of six types, represented by $CoX_3.nNH_3$, where $n = 1, 2, 3, 4, 5$ or 6; they are all coloured salts and distinguished by prefixes signifying the colour characteristic of the series —for example, *xantho-* (yellow), *luteo-* (yellow), *roseo-*, *purpureo-*, *croceo-* (saffron), and *fusco-* (brown).

Cobalt is seen to resemble iron in many respects, but the cobaltic compounds are much less stable than the ferric compounds. Cobaltous compounds become oxidised to cobaltic compounds only in solutions which are neutral or alkaline, while ferrous compounds are easily oxidised in acid solutions. Both iron and cobalt form remarkable compounds with potassium and cyanogen, iron forming the ferrocyanide, $K_4Fe''Cy_6$, and ferricyanide, $K_3F'''Cy_6$, while cobalt forms the cobalticyanide, $K_3Co'''Cy_6$ (see *Cyanides*). No carbonyl of cobalt has yet been obtained.

NICKEL.

$Ni'' = 58.3$ parts by weight.

231. Nickel owes its value in the useful arts chiefly to its property of imparting a white colour to the alloys of copper and zinc, with which it forms the alloy known as *German silver*, and to the ease with which it

can be deposited by electrolysis on other metals (electro-plating), as a lustrous and coherent film which is only slowly tarnished by the atmosphere. Dishes and crucibles of this metal are used in the laboratory in many cases as substitutes for those of platinum and silver, though they are, of course, more easily oxidised. It has been found possible to weld sheet nickel upon iron and steel plates, and culinary vessels, &c., have been made of such plates, which are not liable to rust. Steel containing nickel is exceptionally hard. Alloys of copper and nickel are used in coinage. Nickel is very nearly allied to cobalt, and generally occurs associated with that metal in its ores.

Recently a nickel ore has been discovered in Canada, which consists of magnetic iron pyrites (Fe_3S_4) in which nickel takes the place of some 3–8 per cent. of the iron. This promises to become the most important ore of nickel, though at present the mineral *garnierite*, a silicate of nickel and magnesium found in New Caledonia, furnishes the largest supply of the metal. The first of these ores contains a little cobalt, but the second is free from that metal. The Saxon and Bohemian ores of nickel contain cobalt, arsenic, sulphur, and iron; the chief are *kupfer-nickel*, NiAs, *nickel glance*, $NiAs_2.NiS_2$, and *nickel blende*, NiS.

In the extraction of metals from ores which contain much iron sulphide, as is always the case with sulphureous nickel ores, advantage is taken of the ease with which iron sulphide can be *roasted* to oxide,* and the oxide fluxed as ferrous silicate by fusion with silica. This method of removing iron may be extended to those nickel ores which contain no sulphur, by heating them with gypsum and coke, when the iron becomes converted into sulphide. When the iron has been removed, a mixture (*matte*) of the sulphides of nickel and copper (when this is present in the ores) remains. This is completely oxidised by roasting in air,† and the mixture of oxides of nickel and copper is treated with dilute sulphuric acid, which dissolves the copper oxide; the nickel oxide is made into a paste with charcoal, the paste is cut into cubes and heated to reduce the nickel, which retains the shape of the cubes. The commercial metal contains carbon, iron, silicon, and sulphur. The furnace operations necessary for the above process will be understood by reference to the metallurgy of copper.

The arsenical nickel ores are treated as described above for the removal of iron, and the *speiss* thus obtained, consisting essentially of nickel and arsenic, but containing a little cobalt and copper, is treated by a wet method for the separation of the cobalt. This is effected by roasting the speiss to expel most of the arsenic, dissolving in HCl, peroxidising the solution by bleaching-powder, and neutralising with chalk; in this way the iron is precipitated as basic ferric carbonate, and the remaining arsenic as ferric arsenate. H_2S is passed through the solution to precipitate bismuth and copper as sulphides, leaving cobalt and nickel in solution. The latter, having been boiled to expel the excess of H_2S, is neutralised with lime and mixed with bleaching-powder, which precipitates the cobalt as Co_2O_3, leaving NiO in solution, from which it may be precipitated by adding lime; it is reduced as described above. The Co_2O_3 becomes Co_3O_4 when ignited.

Mond's process for extracting nickel depends on the fact that when the finely divided metal is heated in a current of CO at 50°–100 C. it is volatilised in the form of nickel carbonyl (see below), and thus separated from any other metals, &c., which may accompany it. The nickel

* $2FeS_2+O_{11}=Fe_2O_3+4SO_2$. † $NiS+O_3=NiO+SO_2$.

carbonyl vapour is then heated in another vessel, whereby it is decomposed and deposits its nickel.

In practice the finely divided roasted matte or speiss is caused to descend a tower containing hollow shelves heated internally by hot gas to 250° C., where it meets an ascending stream of water-gas. The oxides are thus reduced to metal, and the material is next conveyed to the top of a second tower, not heated, in descending which it meets a current of gas rich in CO and at a temperature of 50° C. Nickel carbonyl is produced and carried forward as vapour by the gas into an apparatus in which a mass of granules of nickel is kept in motion so that the granules perpetually roll over each other and are prevented from cohering. The temperature of this apparatus being about 200° C., the carbonyl deposits its nickel on the granules while its CO passes on to be used again in the second tower for volatilising more nickel. By keeping the temperature of the volatilising tower as low as possible, the production of iron carbonyl (p. 420) is avoided.

Nickel closely resembles iron, but is less attacked by air and water; its sp. gr. is 8.8, and it melts at 1600° C. At ordinary temperatures it is magnetic, but it loses this property at 250° C.

The *oxides of nickel* correspond in composition with those of cobalt. The salts formed by nickelous oxide (NiO) are usually green, and give bright green solutions. The hydroxide has a characteristic apple-green colour, and does not absorb oxygen from the air like the cobaltous hydroxide. It dissolves in ammonia with a blue colour unchanged by air. The greater facility with which the cobalt is converted into sesquioxide has been applied (as above described) to effect the separation of the two metals. NiO has been found native in octahedral crystals, which have also been obtained accidentally in a copper-smelting furnace; it melts and crystallises in the electric arc.

Ni_3O_4 is obtained by passing moist oxygen over $NiCl_2$ at about 400° C. It has a metallic appearance, and is seen in octahedral crystals under the microscope. It is converted into NiO when heated, and dissolves in hydrochloric acid with evolution of chlorine.

Nickel sulphate ($NiSO_4.H_2O.6Aq$) forms fine green prismatic crystals, the water of constitution in which may be displaced by K_2SO_4 or $(NH_4)_2SO_4$. *Nickel ammonium sulphate*, $NiSO_4.(NH_4)_2SO_4.6H_2O$, is used in electro-plating with nickel. It is almost insoluble in ammonium sulphate solution.

Nickel sulphate may be obtained by dissolving nickel in dilute sulphuric acid. It is isomorphous with the sulphates of Mg, Zn, Fe, and Co. When ammonia is added to its solution, it produces a green precipitate of a basic salt, which dissolves in excess of ammonia to a violet solution, depositing violet crystals of $NiSO_4.4NH_3.2H_2O$.

Four *sulphides of nickel* are known—Ni_2S, NiS, Ni_3S_4 and NiS_2. NiS is found native as *capillary pyrites*, and is obtained as a black precipitate by the action of an alkaline sulphide on a salt of nickel; like cobalt sulphide, it is insoluble in HCl; but ammonium disulphide dissolves it to a dark brown liquid.

Nickel carbonyl, $Ni(CO)_4$, is a colourless liquid (sp. gr. 1.3) which boils at 43° C. and crystallises at −25° C. It is prepared by passing dry CO through a tube containing finely divided nickel which has been reduced from NiO by heating it in hydrogen at 400° C. The $Ni(CO)_4$ is condensed from the excess of CO used by passing the gas through a tube surrounded by ice and salt. It is insoluble in water, but dissolves in alcohol, benzene, and chloroform. Its vapour is decomposed at

150° C. into CO and Ni, which is deposited in the form of a mirror on the sides of the vessel; it is a powerful reducing-agent. Theoretically, it is of great importance as furnishing a volatile compound, by means of which the atomic weight of nickel can be determined.

Nickel is farther removed from iron than cobalt is; its peroxide, Ni_2O_3, shows no disposition to form salts, and it does not form any compound corresponding with ferro- or cobalti-cyanides. It has far less colouring power than cobalt, and its salts are commonly green. In many respects nickel more nearly resembles copper than iron.

Nickel salts are poisonous.

MANGANESE.

$Mn'' = 54.6$ parts by weight.

232. Manganese much resembles iron in several particulars relating both to its physical and chemical characters, and is often found associated, in small quantities, with the compounds of that metal. It is found chiefly as *pyrolusite*, MnO_2, *braunite*, Mn_2O_3, and *manganese spar*, $MnCO_3$. The metal itself has not been applied to any useful purpose. It is obtained either by reducing one of the oxides with charcoal at a very high temperature—when a fused mass, composed of manganese combined with a little carbon (corresponding with cast iron), is obtained, and may be freed from carbon by a second fusion in contact with manganous oxide—by reducing $MnCl_2$ with magnesium, or by igniting a mixture of aluminium powder and manganese oxide (p. 386).

Manganese is grey with a red tinge, hard and brittle, sp. gr. 8, very difficult to fuse (1900° C.), and more easily oxidised than iron, so that it decomposes water when slightly warmed. It is not magnetic unless cooled to − 20° C. It appears to be more volatile than iron.

Manganese dissolves easily in diluted hydrochloric or sulphuric acid, Mn displacing H_2, like Fe and Cr. It resembles iron in its tendency to combine with carbon at a high temperature to form a compound corresponding with cast iron, and in this form the manganese is not oxidised by air. It decomposes water gradually at ordinary temperatures, and boiling water more quickly.

Spiegel-eisen and *ferro-manganese* are alloys containing iron, manganese, and carbon, which are largely used in the production of steel.

233. **Oxides of manganese**, MnO, Mn_2O_3, Mn_3O_4, MnO_2, MnO_3, Mn_2O_7; the first two are bases, the last two anhydrides.

Manganese dioxide or *peroxide*, MnO_2, is the chief form in which this metal is found in nature, and is the source from which all other compounds of manganese are obtained. Its chief mineral form is *pyrolusite*, which forms steel-grey prismatic crystals of sp. gr. 4.9; but it is also found amorphous, as *psilomelane*, and in the hydrated state as *wad*. In commerce, pyrolusite is known as black manganese, or simply manganese, and is largely imported from Germany, Spain, &c., for the use of the manufacturer of bleaching-powder and the glass-maker. It is also used as a cheap source of oxygen, which it evolves when heated to redness, without fusing, leaving the *red oxide of manganese*, Mn_3O_4. The manganese dioxide is an indifferent oxide, and does not combine with acids. Strong HCl, however, dissolves it, giving a brown solution from which water precipitates a brown oxychloride. If the brown

solution, which probably contains Mn_2Cl_6 and $MnCl_4$, be heated, it evolves Cl_2 and becomes colourless $MnCl_2$. Nitric acid is almost without action on MnO_2. Strong sulphuric acid evolves oxygen from it; $MnO_2 + H_2SO_4 = MnSO_4 + H_2O + O$. Even dilute sulphuric acid effects the same change if some substance ready to combine with oxygen is added, such as ferrous sulphate or oxalic acid. Hence a mixture of MnO_2 and H_2SO_4 is much used as an oxidising agent, and it will be seen from the above equation that only half the oxygen in the MnO_2 is *available* for purposes of oxidation. It becomes necessary, therefore, to value the commercial black oxide by ascertaining how much $FeSO_4$ a given weight of it will oxidise in the presence of dilute acid, H_2SO_4.

$$2(FeO.SO_3) + MnO_2 + 2(H_2O.SO_3) = Fe_2O_3.(SO_3)_3 + MnO.SO_3 + 2H_2O.$$

When heated in hydrogen, the oxides of manganese are not reduced to the metal, like those of iron, but are converted into MnO.

Manganous oxide, MnO, obtained in this way, is a greenish powder. It has been obtained in transparent emerald-green crystals. It easily absorbs oxygen from the air. It is a basic oxide, dissolving in acids to form the manganous salts. It has been found native in a manganiferous dolomite.

Manganic oxide, or *manganese sesquioxide*, Mn_2O_3, is found in the mineral *braunite* in octahedral crystals. By its general appearance it might be mistaken for MnO_2, but it dissolves in moderately strong sulphuric acid, forming a red solution of *manganic sulphate*, $Mn_2(SO_4)_3$.

Mn_2O_3 is a feebly basic oxide. It may be obtained by heating any of the oxides of manganese to redness in a current of oxygen, while Mn_3O_4 is formed when any one of the oxides is heated in air. When MnO_2 in very small quantity is added to melted glass, it imparts a purple colour, which is probably due to the formation of a manganic silicate. The amethyst is believed by some to owe its colour to the same cause.

Red oxide of manganese (Mn_3O_4) is the most stable of the oxides of this metal, and is formed when any of the others is heated in air. Thus obtained, it has a brown or reddish colour; but it is found in nature as the black mineral *hausmannite*. In composition it resembles the magnetic oxide of iron, but it seems probable that the true formula is $2MnO.MnO_2$, for when treated with diluted nitric acid it leaves the black hydrated dioxide. Strong sulphuric acid dissolves it to a red liquid containing manganous and manganic sulphates. Dilute sulphuric acid leaves MnO_2 undissolved. HCl dissolves it when heated, evolving Cl and leaving $MnCl_2$.

MnO_3 or *manganic anhydride*, is formed in small quantity by dropping a solution of potassium permanganate in concentrated H_2SO_4 upon dry Na_2CO_3, and condensing the pink cloud which arises, in a tube cooled by ice and salt. It is a red amorphous mass, yielding manganic acid in contact with water.

Permanganic anhydride, Mn_2O_7, is a red oily liquid formed when potassium permanganate is decomposed by strong sulphuric acid; $K_2Mn_2O_8 + 2H_2SO_4 = 2KHSO_4 + Mn_2O_7 + H_2O$. It decomposes slowly, even at common temperatures, evolving oxygen, together with violet vapour of Mn_2O_7. When heated, it decomposes with explosion. It is a most powerful oxidising agent, setting fire to most combustible bodies. In contact with water, it yields *permanganic acid*, $H_2Mn_2O_8$.

Manganous hydroxide, $Mn(OH)_2$, is obtained as a white precipitate when an alkali is added to a manganous salt, out of contact with air. When exposed to air it rapidly becomes brown, forming manganic hydroxide.

Manganic hydroxide, $Mn_2O_2(OH)_2$, may be regarded as Mn_2O_3, in which O has been exchanged for $(OH)_2$, or as $Mn_2O_3.H_2O$, hydrated manganese sesquioxide. It is found in dark grey prismatic crystals, as *manganite*, associated with MnO_2, from which it differs by giving a brown instead of a black streak on unglazed earthenware. Moreover, on boiling it with dilute nitric acid, part of it is dissolved as manganous nitrate, leaving a hydrated manganese dioxide, which dissolves to a brown solution when thoroughly washed. A hydrated manganese dioxide is also precipitated when chloride of lime is added to a manganese salt.

Manganic acid, H_2MnO_4, has not been isolated, but several man-

ganates are known, which are isomorphous with the chromates and sulphates.

Potassium manganate, K_2MnO_4, is formed when MnO_2 is fused with potash; $3MnO_2 + 2KOH = K_2MnO_4 + Mn_2O_3 + H_2O$. If an oxidising agent, such as air or nitre, be present, the Mn_2O_3 is also converted into K_2MnO_4; $Mn_2O_3 + 4KOH + O_3 = 2K_2MnO_4 + 2H_2O$. The extraction of oxygen from air upon this principle has been described at p. 39.

Sodium manganate (Na_2MnO_4), obtained by heating manganese dioxide with sodium hydroxide under free exposure to air, is employed in a state of solution in water, as *Condy's green disinfecting fluid*. It is also used as a bleaching-agent, and in the preparation of oxygen at a cheap rate. The manganates of potassium and sodium dissolve in water containing potash or soda, forming green liquids, but when dissolved in pure water they are decomposed, yielding the red permanganates—

$$3Na_2MnO_4 + 2H_2O = Na_2Mn_2O_8 + MnO_2 + 4NaOH.$$

Barium manganate forms the pigment known as *Cassel green*.

Manganous acid, of which MnO_2 would be the anhydride, might be expected to exist, but is not known. When $Mn(OH)_2$ is oxidised in presence of an alkali, the resulting brown substance contains more or less of the alkali combined with MnO_2. These compounds are known as *manganites—e.g.*, $CaO.MnO_2$.

Permanganic acid, $H_2Mn_2O_8$, has been obtained in a hydrated crystalline state by decomposing the barium permanganate with sulphuric acid, and evaporating the solution *in vacuo*. It is a brown substance, easily dissolving in water to a red liquid, which is decomposed at about 90° F. (32° C.), evolving oxygen, and depositing manganese dioxide.

Potassium permanganate, $K_2Mn_2O_8$, forms rhombic prisms isomorphous with the perchlorate, $KClO_4$, on which account it is sometimes written $KMnO_4$. It dissolves in 20 parts of cold water, forming a purple solution, which becomes green K_2MnO_4 by contact with many substances capable of taking up oxygen. When crystallised permanganate is heated to 240° C. it gives manganate—

$$K_2Mn_2O_8 = K_2MnO_4 + MnO_2 + O_2.$$

It is largely used in many chemical operations. In order to prepare it, 4 parts of finely powdered manganese dioxide are intimately mixed with 3½ parts of $KClO_3$, and 5 parts of KOH dissolved in a very little water. The pasty mass is dried, and heated to dull redness for some time in an iron tray or earthen crucible. The potassium chlorate imparts the required oxygen. On treating the cool mass with water, potassium manganate is dissolved, forming a dark green solution. This is diluted with water, and a stream of CO_2 passed through it so long as any change of colour is observed: $3K_2MnO_4 + 2CO_2 = K_2Mn_2O_8 + MnO_2 + 2K_2CO_3$. The precipitated MnO_2 is allowed to settle, and the clear red solution poured off and evaporated to a small bulk. On cooling, it deposits prismatic crystals of the permanganate ($K_2Mn_2O_8$), which are red by transmitted light, but reflect a dark green colour. The K_2CO_3, being much more soluble in water, is left in the solution.

Potassium permanganate is remarkable for its great colouring power, a very small quantity of the salt producing an intense purplish-red colour in a large quantity of water. Its solution in water is very easily decomposed and bleached by substances having an attraction for oxygen, such as sulphurous acid or a ferrous salt. If a very small piece of iron wire be dissolved in diluted sulphuric acid, the solution of ferrous sulphate so produced will decolorise a large volume of weak solution of the permanganate, being converted into ferric sulphate—

$$K_2Mn_2O_8 + 10FeSO_4 + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O.$$

or $$K_2O.Mn_2O_7 + 10(FeO.SO_3) + 8(H_2O.SO_3) = K_2O.SO_3 + 2(MnO.SO_3) + 5(Fe_2O_3.3SO_3) = 8H_2O,$$

which shows that the molecule of $K_2Mn_2O_8$ has 5 atoms of oxygen *available* for purposes of oxidation.

This decomposition forms the basis of a valuable method for determining the proportion of iron in its ores.

Many organic substances are easily oxidised by potassium permanganate, and this is the case especially with the offensive emanations from putrescent organic matter. Hence it is extensively used, under the name of *Condy's red disinfecting fluid*, in cases where a solid or liquid substance is to be deodorised.

The oxidising power of potassium permanganate is effectively illustrated by pouring a little glycerine into a cavity made in a small heap of the powdered crystals on a porcelain crucible lid; the glycerine slowly sinks into the permanganate, and after a minute or two bursts into vivid combustion.

An alkaline solution of the permanganate is sometimes used as an oxidising agent, since it parts with oxygen when boiled with oxidisable substances, becoming green from the production of manganate—

$$K_2Mn_2O_8 + 2KOH = 2K_2MnO_4 + H_2O + O.$$

Sodium permanganate, $Na_2Mn_2O_8$, is often used as a disinfectant, being cheaper than the potassium salt. It is made by heating MnO_2 with NaOH, in a flat vessel, exposed to air, for 48 hours, to dull redness; the mass is boiled with water to convert the manganate into permanganate; $3Na_2MnO_4 + 2H_2O = Na_2Mn_2O_8 + MnO_2 + 4NaOH$.

234. There appear to be three *chlorides of manganese* corresponding with three of the oxides, viz., $MnCl_2$, Mn_2Cl_6, and $MnCl_4$; but only the first is obtainable in the pure state, the others forming solutions which are easily decomposed with evolution of chlorine. There is also some evidence of the existence of a chloride $MnCl_7$.

By dissolving potassium permanganate in oil of vitriol, and adding fragments of fused sodium chloride, a remarkable greenish-yellow gas is obtained, which gives purple fumes with moist air, and is decomposed by water, yielding a red solution which contains hydrochloric and permanganic acids. It, therefore, must contain manganese and chlorine, and is sometimes regarded as the perchloride ($MnCl_7$); but it is more probably an oxychloride of manganese (see *Chlorochromic acid*). Care is required in its preparation, which is sometimes attended with explosion.

The *manganous chloride* ($MnCl_2$) is obtained in large quantity as a waste product in the preparation of chlorine for the manufacture of bleaching-powder. Since there is no useful application for it, the manufacturer sometimes reconverts it into the black oxide by *Weldon's process* (see p. 170). As the native binoxide always contains iron, the liquor obtained by treating it with HCl contains ferric chloride (Fe_2Cl_6) mixed with $MnCl_2$. In order to separate the iron, advantage is taken of the circumstance that sesquioxides are weaker bases than the protoxides, so that if a small proportion of lime or chalk be added to the solution, the iron may be precipitated as ferric oxide, without decomposing the chloride of manganese; $Fe_2Cl_6 + 3CaO = Fe_2O_3 + 3CaCl_2$.

After separating the Fe_2O_3, *an excess* of lime is added and air blown through the mixture at about 150° F., when the white precipitate of MnO, formed at first, absorbs the oxygen, and becomes a black compound of MnO_2 with lime, which is used over again for the preparation of chlorine. Unless the lime is added in excess, only $MnO.MnO_2$ is formed, so that the excess of lime displaces the MnO and allows it to be converted into MnO_2. In another process Weldon employs magnesia instead of lime, with the view of afterwards recovering the chlorine

from the chloride of magnesium, in the form of hydrochloric acid (see p. 348), and using the magnesia over again.

Manganous sulphate, $MnSO_4.H_2O.6Aq$, isomorphous with green vitriol, forms faintly pink crystals easily soluble in water. It is prepared by adding strong H_2SO_4 to MnO_2, heating the paste to redness to decompose any ferric sulphate, extracting with water, precipitating the last traces of iron by adding manganous carbonate, filtering, and crystallising. Manganous sulphate is employed by the dyer and calico-printer in the production of black and brown colours. Crystals have been obtained of $MnSO_4.H_2O.4Aq.$, isomorphous with copper sulphate.

Manganous sulphide, MnS, occurs as *manganese blende* in steel-grey masses. It may be obtained as a greenish powder by heating any of the oxides of manganese in a current of H_2S. When precipitated by alkaline sulphides from manganese salts, it has a pink colour and contains water. When the pink precipitate is boiled with an excess of alkali sulphide, it becomes a green crystalline powder, $3MnS.H_2O$. The manganous sulphide has a tendency to form soluble compounds with the alkali sulphides, so that a solution of manganese often requires boiling with ammonium sulphide before a precipitate is formed. It dissolves easily in HCl. *Manganese disulphide*, MnS_2, is found, in crystals belonging to the regular system, as *Hauerite*, in Hungary.

Manganese, though more nearly allied to iron than to any other metal, is parted from it by the greater stability of the manganous salts, which are less easily oxidised than the ferrous salts, as well as by the far greater stability of the manganates than of the ferrates, and by the existence of permanganates, which have no parallel in the iron series.

The chlorides of manganese give a green colour to a colourless flame.

CHROMIUM.

Cr = 51.7 parts by weight.

235. This metal derives its name from *χρῶμα, colour*, in allusion to the varied colours of its compounds, upon which their uses in the arts chiefly depend. It is comparatively seldom met with, its principal ore being the *chrome-iron ore* ($FeO.Cr_2O_3$), which is remarkable for its resistance to the action of acids and other chemical agents.* It is chiefly found in the Shetland Islands, Sweden, Russia, Hungary, and the United States, and is imported for the manufacture of **bichromate of potash** ($K_2O.2CrO_3$), which is one of the chief commercial compounds of chromium. The ore is first heated to redness and thrown into water, in order that it may be easily ground to a fine powder, which is mixed with carbonate of potash, chalk being added to prevent the fusion of the mass, and strongly heated in a current of air on the hearth of a reverberatory furnace, the mass being occasionally stirred to expose a fresh surface to the air. The ferrous oxide is thus converted into ferric oxide, and the oxide of chromium (Cr_2O_3) into potassium chromate (K_2CrO_4); $2(FeO.Cr_2O_3) + 4K_2CO_3 + O_7 = Fe_2O_3 + 4K_2CrO_4 + 4CO_2$. Nitre is sometimes added to hasten the oxidation. On treating the mass with water, a yellow solution of potassium chromate is obtained, which is drawn off from the insoluble residue of ferric oxide and lime, and mixed with a slight excess of acid, *e.g.*, nitric acid—

$$2(K_2CrO_4) + 2HNO_3 = K_2Cr_2O_7 + 2KNO_3 + H_2O.$$

The solution, when evaporated, deposits anhydrous, red, tabular crystals of bichromate of potash (potassium dichromate), which dissolve in

* There appear to be four types of chrome-iron ore, viz., $FeO.Cr_2O_3$, $2FeO.Cr_2O_3$, $3FeO.2Cr_2O_3$, and $2FeO.3Cr_2O_3$.

10 parts of cold water, forming an acid solution. It is from this salt that the other compounds of chromium are immediately derived.

Metallic chromium has received no useful application. It is obtained by reducing chromic chloride with zinc (or magnesium) at a high temperature, and removing the excess of zinc with dilute nitric acid. Or Cr_2O_3 may be reduced by aluminium at a high temperature (p. 386). It has a grey colour, is about as heavy as iron (sp. gr. 6.8), is extremely hard, and less fusible (about 3000° C.) than platinum. It resembles aluminium in not being attacked by nitric acid, very readily becoming passive (p. 416) therein, but HCl dissolves it, yielding chromous chloride, $CrCl_2$, a property which connects chromium with iron. Chromium, like aluminium, is attacked by the alkali hydroxides at high temperatures, evolving hydrogen and producing chromates. By the action of sodium on chromic chloride the metal has been obtained in octahedral crystals, which are not dissolved even by nitro-hydrochloric acid.

236. **Oxides of chromium.**—Three oxides of chromium are known in the separate state—*chromic oxide*, Cr_2O_3, *chromium dioxide*, CrO_2, and *chromic anhydride*, CrO_3. *Monoxide of chromium* or *chromous oxide* (CrO) is known in the hydrated state, and *perchromic acid* ($H_3Cr_2O_8$) is believed to exist in solution. The chromous salts correspond with the ferrous salts, but are much more susceptible of oxidation.

Chromic anhydride (often called *chromic acid*), the most important of these, is obtained by adding to one measure of a solution of potassium dichromate, saturated at 54° C., one measure and a half of concentrated sulphuric acid, by small portions at a time, and allowing the solution to cool, when chromic anhydride crystallises out in fine crimson needles, which are deliquescent, very soluble in water, fusing easily, and decomposed at 250° C. into oxygen and chromic oxide. Chromic anhydride is a powerful oxidising agent; most organic substances, even paper, will reduce it to the green chromic oxide. A mixture of potassium dichromate and sulphuric acid is employed for bleaching some oils, the colouring-matter being oxidised at the expense of the chromic acid, and chromic sulphate being produced—

$$K_2Cr_2O_7 + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + O_3 + 4H_2O.$$

The dichromate itself evolves oxygen when heated to bright redness, being first fused (about 400° C.), and afterwards decomposed; $2K_2Cr_2O_7 = 2K_2CrO_4 + Cr_2O_3 + O_3$. Heated with strong HCl, it evolves Cl; $K_2Cr_2O_7 + 14HCl = 2KCl + Cr_2Cl_6 + 7H_2O + Cl_6$. The oxidising effect of the potassium dichromate, under the action of light, upon gelatine and albumin, receives very important applications in photography.

Sodium dichromate, $Na_2Cr_2O_7.2H_2O$, is much more soluble than the potassium salt, requiring only an equal weight of water; it is now often substituted for $K_2Cr_2O_7$, being similarly prepared, and containing, of course, a higher percentage of available oxygen owing to the lower atomic weight of sodium.

Chromic acid, H_2CrO_4, is not known in the pure form. Its salts, the chromates, are isomorphous with the sulphates.

Chromate of potash, or *normal potassium chromate* ($K_2O.CrO_3$ or K_2CrO_4), is formed by adding potassium carbonate to the red solution of potassium dichromate until its red colour is changed to a fine yellow, when it is evaporated and allowed to crystallise. It forms yellow

prismatic crystals, having the same form as those of potassium sulphate, and is five times as soluble in water as the dichromate is, yielding an alkaline solution, which is partly decomposed by evaporation, with formation of the dichromate. Acids, even carbonic, change its solution from yellow to red, from production of dichromate. It becomes red when heated, and yellow again on cooling, and fuses without decomposition. Potassium chromate has been found in some yellow samples of saltpetre from Chili. No compound corresponding with $KHSO_4$ is known.

Trichromate of potash ($K_2O.3CrO_3$) has been obtained in red crystals by adding nitric acid to the dichromate.

It will be observed that the chromates of potassium are rather exceptional salts. The yellow or normal chromate, K_2CrO_4, is formed upon the model of *imaginary* chromic acid, H_2CrO_4. The red chromate, or potassium dichromate, is not a true acid salt, for it contains no hydrogen; it is sometimes called *anhydro-chromate*, and written $K_2CrO_4.CrO_3$. The trichromate would be $K_2CrO_4.2CrO_3$.

Barium chromate, $BaCrO_4$, is used in painting, as *yellow ultramarine*, being precipitated by potassium chromate from barium chloride; it is insoluble in acetic acid; 1 million parts of H_2O dissolve 15 parts of $BaCrO_4$ at 18° C.

Chrome yellow is the *chromate of lead* ($PbCrO_4$), prepared by mixing dilute solutions of lead acetate and potassium chromate. The precipitate is insoluble in acetic acid. It is largely used in painting and calico-printing, and by the chemist as a source of oxygen for the analysis of organic substances, since, when heated, it fuses to a brown mass, which evolves oxygen at a red heat. Chrome yellow being a poisonous salt, its occasional use for colouring confectionery is very objectionable. Chromate of lead in prismatic crystals forms the rather rare *red lead ore of Siberia*, in which chromium was first discovered.

Orange chrome is a *basic chromate of lead* ($PbCrO_4.PbO$), and may be obtained by boiling the yellow chromate with lime; $2(PbCrO_4) + CaO = PbCrO_4.PbO + CaCrO_4$. The calico-printer dyes the stuff with yellow chromate of lead, and converts it into orange chromate by a bath of lime-water. Chrome-orange is also made by precipitating a lead salt with a weak alkaline solution of potassium chromate, which gives a mixture of the two chromates of lead.

Silver chromate, Ag_2CrO_4, is obtained as a red crystalline precipitate when silver nitrate is added to potassium chromate. When $K_2Cr_2O_7$ is added gradually to $AgNO_3$, a scarlet precipitate of *silver dichromate*, $Ag_2Cr_2O_7$, is obtained; and if this be boiled with water, it leaves Ag_2CrO_4 in dark green crystals, which become red when powdered.

The colour of the *ruby* (crystallised alumina) appears to be due to the presence of a small proportion of chromic anhydride.

Sesquioxide of chromium, or *chromic oxide* (Cr_2O_3), is valuable as a green colour, especially for glass and porcelain, since it is not decomposed by heat. Being extremely hard, it is used in making razor-strops. It is prepared by heating potassium dichromate with one-fourth of its weight of starch, the carbon of which removes oxygen, leaving a mixture of chromic oxide with potassium carbonate, which may be removed by washing with water. If sulphur be substituted for the starch, potassium sulphate will be formed, which may also be removed by water. When hydrated chromic oxide is strongly heated, it loses its water and exhibits a sudden glow, becoming darker in colour, and insoluble in acids which previously dissolved it easily; in this respect it resembles aluminia and ferric oxide. Like these oxides, the chromic oxide is a feeble base; it is remarkable for forming two classes of salts, having the same composition, but differing in the colour of their solutions, and in some other properties. Thus, there are two modifications of the *chromic sulphate*—the green sulphate, $Cr_2(SO_4)_3.6Aq$, and the violet sulphate, $Cr_2(SO_4)_3.9Aq$. The solution of the latter conducts electricity well and

gives the reactions of a sulphate, but when boiled it becomes green, conducts badly, and gives no precipitate with $BaCl_2$. *Chrome alum* forms dark purple octahedra ($KCr'''(SO_4)_2.12Aq$) which contain the violet modification of the sulphate; and if its solution in water be boiled, its purple colour changes to green, and the solution refuses to crystallise.* It is obtained as a secondary product in certain chemical manufactures, and may be prepared by the action of sulphurous acid gas on a mixture of potassium dichromate and sulphuric acid; $K_2Cr_2O_7 + H_2SO_4 + 3SO_2 = 2KCr(SO_4)_2 + H_2O$. The anhydrous chromic sulphate forms red crystals, which are insoluble in water and acids. *Guignet's green*, used in painting and calico-printing, is hydrated Cr_2O_3 prepared by heating $K_2Cr_2O_7$ with 3 parts of boric acid (when oxygen is evolved) and washing the product until it is free from potassium borate; it generally retains a little boric acid, perhaps as chromic borate. Cr_2O_3 combines with the oxides of the magnesium group of metals to form very insoluble and infusible compounds, crystallising in octahedra, *e.g.*, $ZnO.Cr_2O_3$, $MnO.Cr_2O_3$, $FeO.Cr_2O_3$, which have been termed *chromites*, and are isomorphous with the spinelles (p. 388).

Crystallised Cr_2O_3, prepared by passing chromyl chloride (p. 434) through a red-hot tube, is isomorphous with Al_2O_3 and Fe_2O_3.

Chromic hydroxide, $Cr_2(OH)_6$, is thrown down by alkalies from solutions of chromic salts, such as chrome alum, as a greenish-blue precipitate. It dissolves sparingly in ammonia to a pink solution, from which chromic oxide is precipitated by boiling. Potash dissolves it to a fine green solution, which becomes gelatinous when boiled, from precipitation of chromic oxide. It yields a hydrosol by the dialysis of its solution in $CrCl_3$.

Chromium dioxide, CrO_2.—When potassium dichromate is reduced by nitric oxide or sodium thiosulphate, a brown precipitate is obtained; this is a compound of water with CrO_2, which is left, on heating to 250° C., as a black powder, which evolves oxygen at 300° C., becoming Cr_2O_3. It may be regarded as *chromic chromate*, $Cr_2O_3.CrO_3$.

Chromous oxide (CrO) is not known in the pure state, but is precipitated as a brown hydrate when chromous chloride is decomposed by potash. It absorbs oxygen even more readily than ferrous oxide does, becoming converted into $CrO.Cr_2O_3$, corresponding in composition with the magnetic oxide of iron. Chromous oxide is a feeble base; a double sulphate, $K_2Cr''(SO_4)_2.6Aq$, is known, isomorphous with the corresponding iron salt, $K_2Fe''(SO_4)_2.6Aq$; it has a blue colour, and gives a blue solution, which becomes green when exposed to air.

Perchromic acid ($H_2Cr_2O_8$) is believed to exist as the blue solution obtained by the action of H_2O_2 upon solution of chromic acid, but neither the acid nor its salts have been obtained in a separate state (p. 64). A *sodium perchromate*, $Na_6Cr_2O_{15}.28H_2O$, crystallises from a solution made by adding Na_2O_2 to a thin paste of $Cr_2(OH)_6$ in water. Acids decompose it, the blue colour of perchromic acid being first produced.

237. **Chlorides of chromium.**—The *chromic chloride* ($CrCl_3$) obtained by passing dry chlorine over a mixture of chromic oxide with charcoal, heated to redness in a glass tube, is converted into vapour, and condenses upon the cooler part of the tube in shining leaflets, having a fine violet colour. When heated in air, it is decomposed, evolving Cl, and leaving Cr_2O_3. Very soluble green crystals of $CrCl_3.6Aq$ may be obtained, but the water cannot be expelled without decomposing the chloride. Cold water does not affect $CrCl_3$, but boiling water slowly dissolves it to a green solution resembling that obtained by dissolving Cr_2O_3 in HCl. If a little chromous chloride be added to water in which $CrCl_3$ is suspended, the latter dissolves quickly and with evolution of heat, yielding the green solution, which becomes violet after some time. Only two-thirds of the Cl is precipitated from the green solution by $AgNO_3$ when this is first added.

Chromous chloride ($CrCl_2$) is obtained by heating $CrCl_3$ in hydrogen. It is white,

* Exposure to cold, it is said, again converts it into the crystallisable violet form.

and dissolves in water to form a blue solution, which absorbs oxygen from the air, becoming green. $CrCl_2$ is also formed when chromium is dissolved in HCl. A solution of chromic chloride or sulphate, mixed with HCl, is reduced to chromous chloride by metallic zinc, the liquid becoming greenish blue and giving a pink precipitate of chromous acetate on addition of ammonium acetate, becoming blue when shaken with air. Chromous chloride resembles ferrous chloride in absorbing NO to form a brown compound.

Chromyl chloride, CrO_2Cl_2 (=2 vols.), or chromic oxychloride, formerly called *chlorochromic acid*, bears the same relation to CrO_3 that sulphuryl chloride, SO_2Cl_2, bears to SO_3. It is a brown-red liquid, obtained by distilling 10 parts of NaCl and 17 of $K_2Cr_2O_7$, previously fused together and broken into fragments, with 40 parts of oil of vitriol—

$$K_2Cr_2O_7 + 4NaCl + 3H_2SO_4 = K_2SO_4 + 2Na_2SO_4 + 3H_2O + 2CrO_2Cl_2.$$

It much resembles bromine in appearance, and fumes very strongly in air, the moisture of which decomposes its red vapour, forming chromic and hydrochloric acids; $CrO_2Cl_2 + 2H_2O = H_2CrO_4 + 2HCl$. Its sp. gr. is 1.92, and it boils at 118° C. It is a very powerful oxidising and chlorinating agent, and inflames ammonia and alcohol when brought in contact with them.

It is occasionally used to illustrate the nature of illuminating flames; for if hydrogen be passed through a bottle containing a few drops of it, the gas becomes charged with its vapour, and, if kindled, burns with a brilliant white flame, which deposits a beautiful green film of chromic oxide upon a cold surface. When heated, in a sealed tube, to 190° C., it is converted into a black solid body, according to the equation $3CrO_2Cl_2 = Cl_4 + CrCl_2.2CrO_3$. When $K_2Cr_2O_7$ is gently warmed with HCl, the solution deposits red prisms of $KClCrO_3$, formerly known as *potassium chlorochromate*, which may be regarded as $CrO_2Cl(OK)$, being derived from the at present unknown $CrO_2Cl(OH)$, corresponding with $SO_2Cl(OH)$.

Chromyl fluoride, CrO_2F_2, is another volatile compound of chromium obtained by distilling lead chromate with fluor spar and sulphuric acid; it is a red gas, condensible to a red liquid at a low temperature. Water decomposes it, yielding chromic and hydrofluoric acids. *Chromic fluoride*, $CrF_3.4H_2O$, is a green crystalline powder used as a mordant.

Chromic sulphide (Cr_2S_3) is formed when H_2S is passed over chromic oxide heated to redness. It forms black lustrous scales resembling graphite.

By fusing chromic hydroxide with sodium carbonate and sulphur, *sodium thiochromite*, $Na_2Cr_2S_4$, is obtained as a dark red body insoluble in water, and not easily attacked by hydrochloric or sulphuric acid. Thiochromites of other metals have also been obtained.

Chromium nitride, CrN, has been obtained by heating chromium to redness in nitrogen.

Chromium salts form a series of amines analogous to the cobalt-amines (p. 423).

Chromium is nearly allied to iron by its property of forming chromous and chromic salts, and to manganese through the chromates which correspond and are isomorphous with the manganates, and rival them in colour. Soluble chromium compounds are very poisonous.

238. **Review of iron, cobalt, nickel, manganese, and chromium.**—Many points of resemblance will have been noticed in the chemical history of these metals. They are all capable of decomposing water at a red heat, and easily displace hydrogen from hydrochloric acid. Each of them forms a base by combining with one atom of oxygen, and these oxides produce salts which have the same crystalline form. All these oxides, except that of nickel, easily absorb oxygen from the air, and are converted into sesquioxides. The sesquioxide of nickel is very feebly basic, whilst that of cobalt is slightly more basic; the sesquioxide of manganese is a stronger base, and the basic properties of the sesquioxides of chromium and iron are very decided. Nickel does not exhibit any tendency to form a well-marked acid oxide, but the existence of an acid oxide of cobalt is suspected; and iron, manganese, and chromium

form undoubted acid oxides with three atoms of oxygen. Nickel is only known to form one compound with chlorine; cobalt and manganese form, in addition to their protochlorides, very unstable perchlorides known only in solution, but iron and chromium form very stable volatile perchlorides. The metals composing this group are all divalent in their protoxides and the corresponding salts, and are found associated in natural minerals; this is especially the case with iron, manganese, cobalt, and nickel. They all require a very high temperature for their fusion. Iron and chromium connect this group with aluminium, their sesquioxides being isomorphous with alumina, and their perchlorides volatile like aluminium chloride. In the periodic table (p. 302) Cr falls in group vi., since its highest salt-forming oxide is CrO_3; Mn forms salts corresponding with Mn_2O_7 (permanganates), and is therefore in group vii. Fe, Co, and Ni are placed in group viii., although oxides of the type RO_4 have yet to be discovered.

MOLYBDENUM, Mo=95.3.

239. This metal derives its name from *μολύβδαινα*, *lead*, on account of the resemblance of its chief ore, *molybdenite*, to black lead. Molybdenite, or *molybdenum glance*, is the *disulphide* (MoS_2), and is found chiefly in Bohemia and Sweden; it may be recognised by its remarkable similarity to plumbago, and by its giving a blue solution when boiled with strong sulphuric acid. It is chiefly employed for the preparation of ammonium molybdate, which is used in testing for phosphoric acid. For this purpose the disulphide is roasted in air at a dull red-heat, when SO_2 is evolved, and *molybdic anhydride* (MoO_3) mixed with oxide of iron is left. The residue is digested with strong ammonia, which dissolves the former as *ammonium molybdate*, obtainable in prismatic crystals (NH_4HMoO_4) on evaporation. When a solution of ammonium molybdate is added to a phosphate dissolved in dilute nitric acid, a yellow precipitate of *ammonium phospho-molybdate** is produced, containing molybdic and phosphoric acids combined with ammonia, by the formation of which very minute quantities of phosphoric acid can be detected. If hydrochloric acid be added in small quantity to a strong solution of molybdate of ammonium, the molybdic acid is precipitated, but it is dissolved by an excess of hydrochloric acid, and if the solution be dialysed, the molybdic acid, H_2MoO_4, is obtained in the form of an aqueous solution which reddens blue litmus, has an astringent taste, and leaves a soluble gum-like residue when evaporated. Besides this simple acid, salts of many complex acids are known, recalling the polysilicates. Molybdic anhydride fuses at a red heat to a yellow glass, and may be sublimed in a current of air in shining needles. In contact with dilute hydrochloric acid and metallic zinc, it is converted into a blue compound of the composition $MoO_2.2MoO_3$ (*molybdenum molybdate*) which is soluble in water, but is precipitated on adding a saline solution. *Molybdate of lead* ($PbMoO_4$) is found as a yellow crystalline mineral (*Wulfenite*). When MoO_3 is heated in hydrogen it is successively reduced to MoO_2 and Mo_2O_3 and finally to metal. The *molybdic oxide* (MoO_2) is basic, and forms dark red-brown salts. *Molybdous oxide* (MoO) is obtained by adding an alkali to the solution resulting from the prolonged action of zinc upon a hydrochloric solution of molybdic acid. It is a black, basic oxide which absorbs oxygen from the air.

Metallic molybdenum is obtained by heating a mixture of an excess of MoO_3 with charcoal in the electric furnace. The pure metal is like the best wrought iron. It is of about the same colour and malleability, easily polished and capable of being forged. Its sp. gr. is 9.01 and its melting-point very high. At 600° C. it oxidises slowly in air and volatilises as MoO_3; it is also attacked by halogens at this temperature but not violently. It decomposes steam when hot and is oxidised by hot strong H_2SO_4, by nitric acid and by fused alkalies from which it evolves H, but it is not attacked by HCl. The resemblance to iron extends to its relation to carbon, with which it may be combined by cementation (p. 411) to form a metal of steely properties, hard enough to scratch glass, and capable of being tempered by

* Its composition varies with the conditions; it is commonly $6NH_4.P_2O_5.24MoO_3$.

quenching from 300° C. With a larger proportion of carbon it forms a metal capable of being cast and containing the carbide Mo_2C; the sp. gr. of such metal is about 8.7.

When heated in chlorine Mo yields *molybdenum pentachloride* ($MoCl_5$), which forms a red vapour, and condenses in crystals resembling iodine, soluble in water. A *subchloride* (Mo_3Cl_6), *trichloride* ($MoCl_3$), *tetrachloride* ($MoCl_4$), and several *oxychlorides* are also known. The *trisulphide* (MoS_3) and *tetrasulphide* (MoS_4) of molybdenum are soluble in alkali sulphides.

In addition to the natural sources of molybdenum above mentioned, there may be noticed *molybdic ochre* (an impure molybdic anhydride), and the difficultly fusible masses called *bear*, from the copper works in Saxony, which contain a large amount of molybdenum combined with iron, copper, cobalt, and nickel. Molybdenum has been detected in the mud deposited by the Buxton thermal water.

TUNGSTEN, W = 182.6.

240. *Tungsten* is chiefly found in the mineral *wolfram*, which occurs, often associated with tin-stone, in large brown shining prismatic crystals, which are even heavier than tin-stone (sp. gr. 7.3), from which circumstance the metal derives its name, tungsten, in Swedish, meaning heavy stone. The symbol (W) used for tungsten is derived from the Latin name *wolframium*. Wolfram contains the tungstates of iron and manganese in variable proportions, and may be regarded as an isomorphous mixture of tungstates of iron and manganese $(MnFe)WO_4$. *Scheelite*, tungstate of calcium ($CaWO_4$), and a tungstate of copper are also found.

Tungstate of sodium, $Na_2WO_4.2H_2O$, is employed by calico-printers as a mordant, and is sometimes applied to muslin, in order to render it uninflammable. It is obtained by fusing wolfram with Na_2CO_3, an operation to which tin ores containing this mineral in large quantity are sometimes submitted previously to smelting them. Water extracts the sodium tungstate, which may be crystallised in rhomboidal plates. When a solution of this salt is mixed with an excess of hydrochloric acid, white *hydrated tungstic acid* ($H_2WO_4.Aq$) is precipitated, while hot solutions give a yellow precipitate of H_2WO_4; but if dilute HCl be carefully added to a 5 per cent. solution of sodium tungstate in sufficient proportion to neutralise the alkali, and the solution be then dialysed (p. 278), the sodium chloride passes through, and a pure aqueous solution of tungstic acid is left in the dialyser. This solution is unchanged by boiling, and when evaporated to dryness, vitreous scales, like gelatine, are left, which adhere very strongly to the dish, and redissolve in one-fourth of their weight of water, forming a solution of the very high specific gravity 3.2, which is, therefore, able to float glass. The solution has a bitter and astringent taste, and decomposes Na_2CO_3 with effervescence. It becomes green when exposed to air, from the de-oxidising action of organic dust. When tungstic acid is heated, it loses water, and becomes of a straw-yellow colour, and insoluble in acids. There are at least two modifications of tungstic acid, which bear to each other a relation similar to that between stannic and metastannic acids (*q.v.*).

Barium tungstate has been employed as a substitute for white lead in painting.

The most characteristic property of tungstic acid is that of yielding a blue oxide ($WO_2.2WO_3$), when placed in contact with HCl and metallic zinc.

A very remarkable compound containing tungstic acid and soda is obtained when *sodium ditungstate* ($Na_2W_2O_7.4H_2O$) is fused with tin. If the fused mass be treated with strong KOH, to remove free tungstic acid, washed with water, and treated with HCl, yellow, lustrous, cubical crystals, probably $Na_2O.WO_2.2WO_3$, are obtained, which are remarkable, among sodium compounds, for their resistance to the action of water, of alkalies, and of all acids except HF. This salt is called *gold-* or *saffron-bronze*. The corresponding potassium salt is *violet-* or *magenta-bronze*.

The *tungstoborates* are remarkable salts, containing WO_3 and B_2O_3, combined with metallic oxides. Their solutions have a very high specific gravity: that of *cadmium tungstoborate* has the sp. gr. 3.6, and is used to effect the mechanical separation of minerals of different specific gravities. Thus, a diamond (sp. gr. 3.5) would float; whilst a white sapphire (sp. gr. 4.0) would sink in the solution. *Tungstosilicates* also exist.

Tungsten trioxide, WO_3, is obtained by decomposing metallic tungstates with nitric acid, and heating the tungstic acid thus precipitated. It is a canary yellow powder, becoming orange when heated and yellow again on cooling.

The *tungsten dioxide* (WO_2) appears to be an indifferent oxide, and is obtained

by reducing tungstic anhydride with hydrogen at a low red heat, when it forms a brown powder, which is dissolved by boiling in solution of potash, hydrogen being evolved, and potassium tungstate formed.

Metallic tungsten is obtained by reducing tungstic anhydride with charcoal (or hydrogen) at a white heat. It may also be obtained by igniting a mixture of WO_3 and aluminium powder, but in order to obtain the necessarily high temperature the mixture must be moistened with about ½ of its volume of liquid air. It is an iron-grey infusible metal of sp. gr. 18.7, very hard, very infusible, not affected by hydrochloric or diluted sulphuric acid, but converted into tungstic acid by the action of nitric acid. Tungsten dissolved in about 20 times its weight of fused steel increases the hardness of the steel without diminishing its tenacity.

When tungsten is heated in chlorine, the *tungstic chloride* (WCl_6) sublimes in bronze-coloured needles. When gently heated in hydrogen, it is converted into the tetrachloride (WCl_4), but if its vapour be mixed with hydrogen and passed through a glass tube heated to redness, metallic tungsten is obtained in a form in which it is not dissolved even by aqua regia, though it may be converted into potassium tungstate by potassium hypochlorite mixed with potash in excess. WCl_6 is also obtained in steel-blue needles, together with $WOCl_4$ and WO_2Cl_2 by the action of PCl_5 on WO_3.

Tungsten disulphide (WS_2) is a black crystalline substance resembling plumbago, obtained by heating a mixture of potassium ditungstate with sulphur, and washing with hot water. *Tungsten trisulphide* (WS_3) is a sulphur-acid, obtainable as a brown precipitate by dissolving tungstic acid in an alkaline sulphide, and precipitating by an acid.

Both MoO_3 and WO_3 form a number of complex salts with the alkali oxides and the pentoxides of As, P, and V. These are the *tungsto-* and *molybdo- arsenates*, *phosphates*, and *vanadates*.

URANIUM, U = 237.7.

241. This metal occurs in the *pitchblende* ($UO_2.2UO_3$) of Cornwall, It is not used in the metallic state, but in the form of the black oxide, $UO_2.UO_3$, and of *sodium uranate*, $Na_2U_2O_7.6H_2O$ (*uranium yellow*), for imparting black and yellow colours respectively to glass and porcelain.* The latter compound is prepared from pitchblende by roasting the mineral with lime, decomposing the calcium uranate thus formed with sulphuric acid, and treating the solution of uranyl sulphate with sodium carbonate. This precipitates the foreign metals and the $Na_2U_2O_7$, which redissolves in the excess of sodium carbonate, and is precipitated by neutralisation with sulphuric acid and boiling.

Uranium forms two oxides, UO_2, a basic oxide known as *uranyl*, and UO_3, an acid oxide. Pitchblende (the green oxide) and the black oxide may be regarded as uranyl diuranate and uranyl uranate respectively. Of the uranyl (also called uranic) salts, the *nitrate*, $UO_2(NO_3)_2.6H_2O$, and *acetate*, $UO_2Ac_2.2H_2O$, are used as laboratory reagents, and in photographic printing, for which they are fitted by the fact that they are reduced by light in contact with organic matter to *uranous* salts, corresponding with the base, UO. These latter salts have been but little studied, but they give a brown precipitate with potassium ferricyanide, by which means the photographic print may be developed. Some organic salts of uranyl are decomposed by light without reduction ; thus the oxalate in water evolves CO and CO_2, leaving a precipitate of *uranylhydroxide*, $UO_2(OH)_2$.

Sodium peruranate, $Na_4UO_8.10H_2O$, is obtained by the addition of sodium peroxide to a solution of a uranyl salt. *Uranium tetrachloride*, UCl_4 (which is volatile, so that its vapour density is known), and *uranyl chloride*, UO_2Cl_2, have been prepared. UCl_3 and UCl_5 are also known.

Metallic uranium is prepared by reducing UCl_4 with sodium. It is white and malleable ; sp. gr. 18.7 ; dissolves in acids evolving hydrogen. When reduced from the oxide by carbon it contains 5–13 per cent. of C, is very hard, melts at a temperature higher than the melting-point of platinum, and decomposes water at the ordinary temperature.

There must here be noticed a curious phenomenon first observed in uranium salts, namely, the power possessed by certain substances of emitting radiations which produce the same effect as that of light on a photographic plate and also so influence the air that its conductivity for electricity is increased. Thus if a crystal

* "Uranium glass" exhibits a strong greenish-yellow fluorescence.

of an ordinary uranium salt be placed on a material opaque to light, such as black paper, or to electricity such as glass or aluminium, and the material be laid upon a photographic plate, the position and shape of the crystal will be faithfully recorded as an invisible image capable of development, in the course of a short time varying with the degree of activity. Again, if the crystal be held at a short distance from a charged electroscope this will lose its charge more quickly than it would normally.

It has been shown that uranium nitrate recrystallised from ether is free from this property, indicating that the activity is due to some other substance.

Certain specimens of pitchblende containing bismuth are particularly active, and when the bismuth is extracted the activity is found to have accompanied it, but the radiations differ from those of uranium salts in that they are not deviated by an electro-magnet. It has been supposed that such bismuth contains an element, *polonium*, which is the source of the activity. A second supposed element, *radium*, having great "radio-activity" and closely resembling barium in character, has been detected in pitchblende. The rays from the compounds of this substance colour glass, ozonise oxygen and convert yellow phosphorus into red, besides having the properties already cited for such radiations. The effect of radium radiation on the skin is remarkable, creating painful sores which are slow to heal. This effect has been shown to occur even through the clothing and when the absolute quantity of radium is very small.

Thorium compounds also possess radio-activity, and it has been shown that both in this case and that of radium part of the radiation is an emanation of material particles which may be deposited on other substances, especially if they be negatively electrified, rendering them also radio-active temporarily. A negatively electrified platinum wire becomes radio-active when it has been exposed to the air for some time. At present these phenomena must be regarded as inexplicable, and the existence of new elements cannot be safely deduced from the observation of such properties.

Review of the chromium family of metals.—The members of this family, chromium, molybdenum, tungsten, and uranium, exhibit great similarity in their tendency to form acid oxides of the type RO_3, and oxychlorides of the type RO_2Cl_2. They also enter into the composition of many complex salts analogous to the phospho-molybdates and the boro-tungstates. Sulphur, selenium, and tellurium belong to the same group, and form oxyacids of the same type.

BISMUTH.

$Bi''' = 206.9$ parts by weight.

242. Bismuth, though useful in various forms of combination, is too brittle to be employed in the pure metallic state. It is readily distinguished from other metals by its peculiar reddish lustre and its highly crystalline structure, which is very perceptible upon a freshly broken surface; large crystals (apparently cubes) of bismuth are easily obtained by melting a few ounces in a crucible, allowing it to cool till a crust has formed upon the surface, and pouring out the portion which has not yet solidified, when the crystals are found lining the interior of the crucible. It is isomorphous with antimony. It is somewhat lighter than lead (sp. gr. 9.8), and volatilises more readily at high temperatures. It is less volatile than antimony, and burns like it in air.

Unlike most other metals, bismuth is found chiefly in the metallic state, disseminated in veins, through gneiss and clay-slate. The chief supply is derived from the mines of Schneeberg, in Saxony, where it is associated with the ores of cobalt. Native bismuth, together with the oxides and sulphides, is found abundantly in Bolivia and Australia, accompanied by tin-stone and sometimes by silver and gold.

In order to extract the metal from the masses of earthy matter through which it is distributed, advantage is taken of its very low fusing-point (268° C.). The ore is broken into small pieces, and introduced into iron cylinders which are fixed in an inclined position over a furnace (Fig. 226). The upper opening of the cylinders, through which the ore is introduced, is provided with an iron door, and the lower opening is closed with a plate of fire-brick perforated for the escape of the metal, which flows out, when the cylinders are heated, into iron receiving pots, which are kept hot by a charcoal fire.

Fig. 226.—Extraction of bismuth.

Commercial bismuth generally contains arsenic, copper, sulphur, and silver; it is sometimes *cupelled* in the same manner as lead, in order to extract the silver, the oxide of bismuth being afterwards again reduced to the metallic state by heating it with charcoal. Pure bismuth dissolves entirely and easily in diluted nitric acid (sp. gr. 1.2); but if it contains arsenic, a white deposit of bismuth arsenate is obtained. Hydrochloric and diluted sulphuric acids will not attack bismuth.

The chief use of bismuth is in the preparation of certain alloys with other metals. Some kinds of type metal and stereotype metal contain bismuth, which confers upon them the property of expanding in the mould during solidification, so that they are forced into the finest lines of the impression.

This metal is also remarkable for its tendency to lower the fusing-point of alloys, which cannot be accounted for merely by referring to the low fusing-point of the metal itself. Thus, an alloy of 2 parts bismuth, 1 part lead, and 1 part tin, fuses below the temperature of boiling water, although the most fusible of the three metals, tin, requires a temperature of 227° C. An alloy of this kind is used for soldering pewter. *Wood's fusible alloy* consists of 4 of Bi, 2 of Pb, 1 of Sn, and 1 of Cd; it melts at 60.5° C. Bismuth is also employed, together with antimony, in the construction of thermo-electric piles.

243. **Oxides of bismuth.**—There are four oxides, BiO, Bi_2O_3, Bi_3O_4, and Bi_2O_5.

Bismuth suboxide, BiO, is a black powder obtained by heating bismuth oxalate in CO_2. When bismuthic chloride mixed with stannous chloride is added to an excess of potash, a black precipitate is obtained, alleged by some to be the suboxide, by others metallic bismuth.

Bismuthous oxide, Bi_2O_3, is the basic and most important oxide. It is formed when bismuth is heated in air, or when bismuth nitrate is decomposed by heat, and is a yellow powder becoming brown when heated, and fuses easily. Bismuthous oxide forms the rare mineral *bismuth-ochre*. This oxide of bismuth is obtained in fine needles by precipitating a boiling solution of a bismuth salt with potash.

Bismuthic anhydride, Bi_2O_5, is formed when Bi_2O_3 is suspended in a strong solution of potash through which chlorine is passed, when a brown substance is formed which, when treated with warm strong HNO_3, yields bismuthic acid ($HBiO_3$) as a red powder, which becomes brown at 120° C., losing H_2O and becoming Bi_2O_5. When further heated, it loses O and becomes Bi_2O_4 or $Bi_2O_3.Bi_2O_5$. When heated with acids it also evolves O, and forms salts of Bi_2O_3.

Bismuth hydroxide, $Bi(OH)_3$, is obtained as a white precipitate when a caustic alkali is added to a bismuth salt; it does not dissolve in excess of alkali. Acted on by chlorine in the alkaline liquid, it becomes dark brown $HBiO_3$.

Bismuthic acid, $HBiO_3$, the analogue of HNO_3, is formed when basic bismuth nitrate is fused with potash, in contact with air, until it has become dark brown. On dissolving in dilute nitric acid, $HBiO_3$ is left as a red powder. The bismuthates of the alkali metals are very unstable, being decomposed by water. *Pyrobismuthic acid*, $H_4Bi_2O_7$, is said to have been obtained.

244. The only two salts of bismuth which are known in the arts are the **basic nitrate** (*trisnitrate of bismuth*, or *flake-white*) and the **oxychloride of bismuth** (*pearl-white*). The preparation of these compounds illustrates one of the characteristic properties of the salts of bismuth, viz., the facility with which they are decomposed by water with the production of insoluble basic salts.

If bismuth be dissolved in nitric acid, it becomes bismuth nitrate, $Bi(NO_3)_3$, and this may be obtained in prismatic crystals containing 5Aq. If the solution be mixed with a large quantity of water, it deposits a precipitate of *flake-white*, $Bi(NO_3)_3.2Bi(OH)_3$, or $Bi(OH)_2NO_3$, the remainder of the nitric acid being left in the solution—

$$Bi(NO_3)_3 + 2H_2O = Bi(OH)_2NO_3 + 2HNO_3.$$

The basic nitrate, when long washed, becomes $Bi(OH)_3$. It is a crystalline powder, which is acid to moist test-paper. It is used as a paint and cosmetic, and in enamelling porcelain.

Pearl-white has the composition 6BiOCl.Aq, and is obtained by dissolving bismuth in nitric acid, and pouring the solution into water in which common salt has been dissolved.

Bismuthite, which is, next to native bismuth, the most important of the bismuth ores, is composed of $3Bi_2O_3.CO_2.H_2O$.

Bismuthic chloride, $BiCl_3$ (=2 vols.), may be distilled over when bismuth is heated in a current of dry chlorine; it is a deliquescent, fusible, volatile, crystalline solid, easily dissolved by a small quantity of water, but decomposed by much water, with formation of the above-mentioned *oxychloride of bismuth*; $BiCl_3 + H_2O = BiOCl + 2HCl$. This compound is so insoluble in water that nearly every trace of bismuth may be precipitated from a moderately acid solution of the trichloride by adding much water.

Bismuth tri-iodide, BiI_3, is obtained as a dark brown precipitate when potassium iodide is added to a solution of a bismuthic salt. If the solution be dilute or very acid, a red or yellow colour is produced, without precipitation, and if a solution of a lead salt be added to this, a brown or red precipitate of a double iodide of bismuth and lead is produced, which dissolves in hot dilute HCl, and separates in minute crystals, like bronze powder, on cooling.

Bismuthous sulphide (Bi_2S_2) is sometimes found in nature, but more frequently *bismuthic sulphide* (Bi_2S_3) or *bismuth glance*, which occurs in dark grey lustrous prisms isomorphous with native sulphide of antimony. Bi_2S_3 is also obtained as a brown precipitate by the action of hydrosulphuric acid upon bismuthic salts. Bismuthic sulphide is not soluble in diluted sulphuric or hydrochloric acid, but dissolves easily in nitric acid. *Bolivite* is an oxysulphide, $Bi_2S_3.Bi_2O_3$.

ANTIMONY.

$Sb''' = 119$ parts by weight.

245. Antimony is nearly allied to bismuth in its physical and chemical characters. It is even harder and more brittle than that metal, being easily reduced to powder. Its highly crystalline structure is another very well-marked feature, and is at once perceived upon the surface of an ingot of antimony, where it is exhibited in beautiful fern-like markings (*star antimony*). Its crystals belong to the same system (the rhombohedral) as those of bismuth and arsenic. It is much lighter than bismuth (sp. gr. 6.715), and requires a higher temperature (630° C.) to fuse it, though it is more easily converted into vapour, so that, when strongly heated in air, it emits a thick white smoke, the vapour being oxidised. Like bismuth, it is but little affected by hydrochloric or dilute sulphuric acid, but nitric acid oxidises it, though it dissolves very little of the metal, the greater part being left in the form of antimonic acid. The best method of dissolving antimony is to boil it with hydrochloric acid and to add nitric acid, or some other oxidising agent, by degrees. The metal decomposes steam at a red heat.

Antimony is chiefly found in nature as *grey antimony ore*, *stibnite*, which is a sulphide of antimony (Sb_2S_3), occurring in Cornwall, but much more abundantly in Hungary, in veins associated with galena, iron pyrites, quartz, and heavy spar. To purify it from these, advantage is taken of its fusibility, the ore being heated upon the hearth of a reverberatory furnace, with some charcoal to prevent oxidation, when the sulphide of antimony melts and collects below the impurities, whence it is run off and cast into moulds. The product is known in commerce as *crude antimony*, and contains sulphides of arsenic, iron, and lead.

To obtain *regulus of antimony*, or metallic antimony, the sulphide is fused in contact with refuse iron (such as tin-plate clippings), when sulphide of iron is formed, and collects as a fused slag upon the surface of the melted antimony; $Sb_2S_3 + Fe_3 = 3FeS + Sb_2$. The antimony always contains a considerable proportion of iron.

To refine it the metal is melted again with sufficient Sb_2S_3 to convert the iron into sulphide. To eliminate sulphur and obtain star antimony, the product must be fused with an alkali sulphide which dissolves the Sb_2S_3, producing a slag consisting mainly of $3Na_2S.Sb_2S_3$, and called *crocus of antimony*.

In some places the antimony ore is roasted to convert the bulk of it into oxide, which is then heated with fresh ore, in order that the mixture may undergo "self-reduction"; $2Sb_2S_3 + 3Sb_2O_4 = Sb_{10} + 6SO_2$.

Antimony is now obtained by leaching the ore with a solution of sodium sulphide, whereby the Sb_2S_3 is dissolved. The solution is then electrolysed, Sb being deposited on the cathode, leaving a solution of sodium sulphide to be used for leaching more ore.

On the small scale, antimony may be extracted from the sulphide by fusing it in an earthen crucible with 4 parts of commercial potassium cyanide, at a moderate heat; or by mixing 4 parts of the sulphide with 3 of bitartrate of potash and 1½ of nitre, and throwing the mixture, by small portions, into a red-hot crucible, when the sulphur is oxidised, and converted into potassium sulphate, by the nitre, which is not present in sufficient quantity to oxidise the antimony, so that the metal collects at the bottom of the crucible.

When tartar-emetic is strongly heated in a closed crucible, an alloy of antimony and potassium is obtained which decomposes water rapidly, and becomes hot when exposed to air.

The brittleness of antimony renders it useless in the metallic state,

except for the construction of thermo-electric piles, where it is in conjunction with bismuth. Antimony is employed, however, to harden several useful alloys, such as type-metal, shrapnel-shell bullets, Britannia metal, and pewter.

Amorphous antimony.—The ordinary crystalline form of antimony may be obtained, like copper and other metals, by electrolysing a solution containing about 7 per cent. of antimonious chloride; but in some cases the antimony is deposited from very strong solutions in an amorphous condition, having properties very different from those of ordinary antimony. One part of tartar-emetic is dissolved in 4 parts of a strong solution of antimony trichloride and the solution is slowly electrolysed. The deposit of antimony which forms upon the cathode has a brilliant metallic appearance, but is amorphous, and not crystalline, like the ordinary metal. Its specific gravity is 5.78. If it be gently heated, scratched or sharply struck, its temperature rises suddenly to about 200° C., and it becomes converted into a form more nearly resembling crystalline antimony. At the same time, however, thick fumes of antimony trichloride are evolved, for this substance is always present in the amorphous antimony to the amount of 5 or 6 per cent.;* so that, as yet, there is not sufficient evidence to establish beyond a doubt the existence of a pure amorphous form of antimony corresponding with amorphous phosphorus, however probable this may appear from the chemical resemblance between these elements.

246. **Oxides of antimony**, Sb_4O_6,† Sb_2O_4, Sb_2O_5.—*Antimonious oxide*, Sb_4O_6, is formed when antimony burns in air (*flowers of antimony*), and is prepared on a large scale by roasting either the metal or the sulphide in air, for use in painting as a substitute for white lead. It is also found in nature as *white antimony ore*, or *valentinite*. Antimonious oxide forms a crystalline powder (sp. gr. 5.56), usually composed of minute prisms having the shape of the rarer form of arsenious oxide (page 268), whilst occasionally it is obtained in crystals similar to those of the common octahedral arsenious oxide, with which, therefore, antimonious oxide is *isodimorphous*. The octahedral form appears to be produced only when the prismatic form is slowly sublimed in a non-oxidising atmosphere. The mineral *exitèle* is prismatic oxide of antimony, and *senarmontite* is the octahedral form of that oxide. When heated in air the oxide assumes a yellow colour, afterwards takes fire, smoulders, and becomes converted into the antimonious antimonate ($Sb_2O_3.Sb_2O_5 = 2Sb_2O_4$), which was formerly regarded as an independent oxide. Sb_4O_6 may be obtained by oxidising antimony with very weak nitric acid, or better, by dissolving antimony sulphide in strong HCl, boiling off all H_2S, diluting largely with water, washing the precipitated oxychloride by decantation till it is no longer acid, and boiling it with a strong solution of sodium carbonate; $4SbOCl + 2Na_2CO_3 = Sb_4O_6 + 4NaCl + 2CO_2$. The oxide is insoluble in water, but acids dissolve it, forming salts, though its basic properties are feeble, and its salts rather ill-defined. A hot solution of hydropotassium tartrate, $HKC_4H_4O_6$, dissolves it, forming *tartar-emetic*, $SbO.KC_4H_4O_6$. Potash and soda are also capable of dissolving it, whence it is sometimes called *antimonious anhydride*, corresponding with nitrous anhydride. Two crystallised *antimonites of sodium* have been obtained, the neutral antimonite $NaSbO_2.6Aq$, and the triantimonite $NaSbO_2.Sb_2O_3.Aq$; the former is sparingly soluble, the latter almost insoluble in water.

* It has been plausibly suggested that the sudden rise of temperature may be due to the presence of an endothermic antimony compound analogous to the so-called chloride of nitrogen, the latter element being connected with antimony by several chemical analogies.

† The vapour density of this oxide shows that its formula cannot be Sb_2O_3, as formerly supposed.

Antimony tetroxide, Sb_2O_4, is important because it is the product of the action of heat upon either of the other oxides in contact with air, so that antimony is often weighed in this form in quantitative analysis. It is readily obtained by boiling antimony with nitric acid, evaporating to dryness, and heating the residue to redness. It is yellow while hot, and becomes white on cooling.

Antimony ash, obtained by roasting the grey sulphide in air, consists chiefly of Sb_2O_4, and is used for preparing other antimony compounds.

Thus, tartar-emetic may be obtained by boiling Sb_2O_4 with hydropotassium tartrate; $Sb_2O_4 + HKC_4H_4O_6 = SbO.KC_4H_4O_6$ (tartar-emetic) $+ HSbO_3$ (antimonic acid). This leads to the belief that Sb_2O_4 is really *antimonyl antimonate*, $SbO.SbO_3$, in which case this formation of tartar-emetic would merely consist in the exchange of SbO for H.

The presence of Sb_2O_4 in Sb_4O_6 can be detected by dissolving in HCl and adding KI, when iodine will be liberated—

$$Sb_2O_4 + 2KI + 8HCl = 2SbCl_3 + 2KCl + 4H_2O + I_2.$$

Antimonic oxide, Sb_2O_5, is formed when antimony is oxidised by nitric acid, and the product well washed and dried at 280° C. It is a yellow powder (sp. gr. 6.5). It will be remembered that As_2O_5 may be obtained in a similar way, but not P_2O_5. Sb_2O_5 is a pale yellow amorphous powder, insoluble in water, and decomposed at 300° C., leaving Sb_2O_4. It is dissolved by potash, forming the antimonate, $KSbO_3$.

Antimonious acid,* $HSbO_2$, corresponding with nitrous acid, is said to have been obtained as $2HSbO_2.3Aq$, in the form of a white precipitate, by decomposing sodium antimonite with nitric acid.

Antimonic acid, $HSbO_3$, corresponding with nitric acid, is precipitated as $HSbO_3.2Aq$ by adding nitric acid to solution of potassium antimonate. It is a white powder, slightly soluble in water, and easily so in potash.

Potassium antimonate, $KSbO_3$, is made by gradually adding 1 part of powdered antimony to 4 parts of nitre fused in a clay crucible. The mass is powdered and washed with warm water to remove the excess of nitre and the potassium nitrite, when the anhydrous potassium antimonate is left; and on boiling this for an hour or two with water, it becomes hydrated, and dissolves. The solution, when evaporated, leaves a gummy mass of *potassium antimonate*, having the composition $2KSbO_3.5Aq$. This dissolves in warm water, and is decomposed by boiling for some time, yielding an acid antimonate, $K_4H_2(SbO_3)_6.9Aq$.

Sodium antimonate, $2NaSbO_3.7Aq$, is prepared like the potassium salt.

Ammonium antimonate, NH_4SbO_3, is obtained as a crystalline powder, insoluble in water, by dissolving $HSbO_3$ in warm ammonia.

A *basic lead antimonate* is used in oil-painting as *Naples yellow*.

Metantimonic acid, $H_4Sb_2O_7$, should really be called pyro-antimonic acid, since it corresponds with pyrophosphoric acid, $H_4P_2O_7$. It is obtained as a white precipitate by decomposing antimonic chloride with water; $2SbCl_5 + 7H_2O = H_4Sb_2O_7 + 10HCl$. It is rather more soluble in water than is antimonic acid, and dissolves in cold ammonia. When heated to 200° C., it is converted into antimonic acid; $H_4Sb_2O_7 = 2HSbO_3 + H_2O$. This resembles the conversion of pyrophosphoric into metaphosphoric acid by the action of the heat. It is said that *orthantimonic acid*, H_3SbO_4, has been isolated.

Potassium metantimonate, $K_4Sb_2O_7$, is made by fusing the antimonate with potash, in a silver crucible; $2KSbO_3 + 2KOH = K_4Sb_2O_7 + H_2O$. On dissolving in water and evaporating, crystals of the metantimonate are obtained, but water decomposes these into potash and *potassium dimetantimonate*, $K_2H_2Sb_2O_7$, which forms a crystalline powder containing 6Aq. It is sparingly soluble in cold water, but dissolves in warm water. The solution forms a valuable test for sodium, which it precipitates in the form of $Na_2H_2Sb_2O_7.6Aq$. When long kept, the solution of potassium dimetantimonate becomes converted into antimonate, which

* Strictly *metantimonious* acid; *orthantimonious* acid, $Sb(OH)_3$, has not been prepared.

does not precipitate sodium; $K_2Sb_2O_7 + H_2O = 2KSbO_3 + 2KOH$. Acids precipitate metantimonic acid, which dissolves in HCl. Nearly all metallic solutions yield precipitates with the potassium dimetantimonate, so that all other metals must be removed from the solution before testing for sodium.

247. **Antimonetted hydrogen**, or *hydrogen antimonide*, SbH_3, is not known in the pure state, but is obtained, mixed with H, when an alloy of antimony with zinc is attacked by dilute sulphuric acid, or when a solution of an antimony salt (tartar-emetic, for example) is poured into a hydrogen apparatus containing zinc and dilute sulphuric acid (see page 272). Its production forms the most delicate test for antimony, as in the parallel case of arsenic, but the one cannot be mistaken for the other, if the following differences be observed. The SbH_3 burns to Sb_4O_6 and H_2O with a *greenish* flame, which deposits a *soot-black* spot upon a porcelain crucible lid (Fig. 192). This spot dissolves when a drop of yellow ammonium sulphide is placed on it with a glass rod, and on evaporation gives an orange film of Sb_2S_3. When the tube through which the gas passes is heated to 150° C. (Fig. 193), metallic antimony is deposited at the heated part, and not beyond it, like arsenic. When the gas is passed into silver nitrate, the antimony is precipitated as black silver antimonide; $SbH_3 + 3AgNO_3 = SbAg_3 + 3HNO_3$ (whereas arsenic passes into solution as arsenious acid, and gives a black precipitate of metallic silver).

Sulphur decomposes SbH_3 in sunlight or at 100° C., but not in the dark: $2SbH_3 + 3S_2 = Sb_2S_3 + 3H_2S$. The reactions with silver nitrate and with sulphur prove the composition of the gas to be SbH_3, so that it is analogous to AsH_3, PH_3, and NH_3.

If the hydrogen antimonide be prepared by the action of dilute sulphuric acid upon an alloy of 2 parts of antimony with 3 parts of zinc, and the first portions collected separately and cooled to −91° C., it solidifies, but on raising the temperature to about −60° it is decomposed, antimony being deposited. This explains why so little of the compound is obtained in the gas made under ordinary conditions.

248. **Chlorides of antimony.**—Chlorine and antimony combine readily with evolution of heat and light; the chlorides are among the most important compounds of this metal.

Trichloride of antimony, or *antimonious chloride*, $SbCl_3$, may be prepared by dissolving powdered antimony sulphide (100 grams) in commercial hydrochloric acid (500 c.c.), adding gradually potassium chlorate (4 grams), filtering from sulphur and distilling. HCl distils first, then a solution of $SbCl_3$ and finally $SbCl_3$ itself, which forms white crystals in the receiver. The trichloride is a soft crystalline solid, whence its old name of *butter of antimony*. It fuses at 73° C. and boils at 223° C. It may be dissolved in a small quantity of water, but a large quantity decomposes it, forming a bulky white precipitate, which is an *oxychloride of antimony*; $SbCl_3 + H_2O = 2HCl + SbOCl$; this is a decomposition similar to that which occurs with PCl_3, $AsCl_3$, and $BiCl_3$. By long washing, $4SbOCl + 2H_2O = 4HCl + Sb_4O_6$. When hot water is added to a hot solution of trichloride of antimony in hydrochloric acid, minute prismatic needles are deposited, containing $Sb_4Cl_2O_5$, and formerly called *powder of Algaroth*. The same body is formed when SbOCl is heated; $5SbOCl = SbCl_3 + Sb_4Cl_2O_5$. Trichloride of antimony is occasionally used in surgery as a caustic; it also serves as a bronze for gun-barrels, upon which it deposits a film of antimony.

Pentachloride of antimony, or *antimonic chloride* ($SbCl_5$), is prepared by heating coarsely powdered antimony in a retort, through which a stream of dry chlorine is passed (Fig. 182), the neck of the retort being fitted into an adapter, which serves to condense the pentachloride. One ounce of antimony will require the chlorine from about 6 oz. of common manganese and 18 oz. (measured) of hydrochloric acid. The pure pentachloride is a colourless fuming liquid of a very suffocating odour; it combines energetically with a small quantity of water, forming a crystalline hydrate, $SbCl_5.4Aq$, but an excess of water decomposes it into hydrochloric and metantimonic acids, the latter forming a white precipitate; $2SbCl_5 + 7H_2O = 10HCl + H_4Sb_2O_7$.

If it be dropped into water kept cool by ice, it yields *antimony oxytrichloride* as a deliquescent crystalline body; $SbCl_5 + H_2O = SbOCl_3 + 2HCl$. Pentachloride of antimony is employed by the chemist as a chlorinating agent; thus, olefiant gas (C_2H_4), when passed through it, is converted into Dutch liquid ($C_2H_4Cl_2$), and carbonic oxide into phosgene gas, the pentachloride of antimony being converted into trichloride. $SbCl_5$ is partially dissociated into $SbCl_3$ and Cl_2 at 140° C. and completely at 200° C., and can only be distilled in chlorine.

The pentachloride of antimony is the analogue of pentachloride of phosphorus, and a *chlorosulphide of antimony* ($SbCl_3S$), corresponding with chlorosulphide of phosphorus, is obtained as a white crystalline solid by the action of hydrosulphuric acid upon pentachloride of antimony.

249. **Sulphides of antimony.**—*Antimonious sulphide*, or *sesquisulphide of antimony* (Sb_2S_3), has been noticed as the chief ore of antimony. It is abundant in Borneo. It is a heavy mineral (sp. gr. 4.63), of a dark grey colour and metallic lustre, occurring in masses which are made up of long prismatic needles. It fuses easily, and may be sublimed unchanged out of contact with air. When melted and suddenly cooled it forms a dark brown amorphous mass of sp. gr. 4.15, which is not a conductor of electricity, whereas the grey form conducts. It is easily recognised by heating it, in powder, with hydrochloric acid, when it evolves the odour of hydrosulphuric acid, and if the solution be poured into water, it deposits an orange precipitate (page 214). This orange sulphide, which is a compound of Sb_2S_3 with water, is also obtained by adding hydrosulphuric acid to a solution of a salt of antimony (for example, tartar-emetic) acidified with HCl. It may be converted into the grey sulphide at 210° C., and becomes black when boiled with HCl in a current of CO_2. The orange variety constitutes the *antimony vermilion*, the preparation of which has been described at p. 232. Native sulphide of antimony is employed, in conjunction with potassium chlorate, in the *friction-tube* for firing cannon; it is also used in *percussion caps*, together with potassium chlorate and mercuric fulminate. Its property of deflagrating with a bluish-white flame, when heated with nitre, renders it useful in compositions for coloured fires.

Glass of antimony is a transparent red mass obtained by roasting antimonious sulphide in air, and fusing the product; it contains about 8 parts of oxide and 1 part of sulphide of antimony. It is used for colouring glass yellow.

Red antimony ore is an oxysulphide of antimony, $Sb_2O_3.2Sb_2S_3$.

Antimonic sulphide (Sb_2S_5) is obtained as a bright orange-red precipitate by the rapid action of H_2S upon a solution of pentachloride of antimony in HCl; it is decomposed by heat into Sb_2S_3 and S_2. When boiled with hydrochloric acid, $Sb_2S_5 + 6HCl = 2SbCl_3 + 3H_2S + S_2$, show-

ing the trivalence of antimony to be stronger than the pentavalence. It is prepared on a large scale under the name of *golden sulphuret of antimony* by boiling Sb_2S_3 with KOH and S, and adding acid to the solution of potassium thioantimonate (*liver of antimony*) thus obtained. It is used for vulcanising india-rubber.

When H_2S acts slowly on $SbCl_5$ a mixture of Sb_2S_5, Sb_2S_3 and S is obtained. In presence of Cr_2Cl_6 more Sb_2S_3 is formed. When exposed to light under water or boiled with water, Sb_2S_5 yields black crystalline Sb_2S_3 and S.

Both Sb_2S_3 and Sb_2S_5 are dissolved by the alkali sulphides, forming *thiometantimonites* (from $HSbS_2$) and *thioantimonates* (from H_3SbS_4) respectively. Thus, like the sulphide of arsenic, they dissolve in alkalies yielding the appropriate oxy-salts and thio-salts; for example, $2Sb_2S_3+4KOH=3KSbS_2+KSbO_2+2H_2O$, and $4Sb_2S_5+24KOH=5K_3SbS_4+3K_3SbO_4+12H_2O$. When the solutions are acidified, all the Sb is precipitated again as sulphide. Even metallic antimony, in powder, is dissolved when gently heated with solution of potassium sulphide in which sulphur has been dissolved, any lead or iron which may be present being left in the residue, so that the antimony may be tested by this process as to its freedom from those metals.

Mineral kermes is a variable mixture of oxide and sulphide of antimony, which is deposited as a reddish-brown powder from the solution obtained by boiling sulphide of antimony with potash or soda. It was formerly much valued for medicinal purposes. *Kermes* was the Arabic name of an insect used in dyeing scarlet.

Schlippe's salt is the sodium thioantimonate ($Na_3SbS_4.9H_2O$), and may be obtained in fine transparent tetrahedral crystals by dissolving Sb_2S_3 in NaOH and adding sulphur. This salt is sometimes used in photography.

Antimonious sulphate, $Sb_2(SO_4)_3$, is formed when antimony is boiled with strong H_2SO_4. It crystallises in needles, which are decomposed by water into a soluble sulphate, and an insoluble basic sulphate.

VANADIUM.*

V = 50.8.

249*a*. This metal was originally discovered in certain Swedish iron ores, but its chief ore is the *vanadate of lead*, which is found in Scotland, Mexico, and Chili. Vanadic acid has also been found in some clays, in the cupriferous sandstone at Perm in Russia, and Alderley Edge in Cheshire; it is contained in some specimens of coal. By treating the vanadate of lead with HNO_3, expelling the excess of acid by evaporation, and washing out the lead nitrate with water, impure *vanadic anhydride* (V_2O_5) is obtained, which may be purified by dissolving in ammonia, crystallising the *ammonium metavanadate* NH_4VO_3, and decomposing it by heat, when vanadic anhydride is left as a reddish-yellow fusible solid, which crystallises on cooling, and dissolves sparingly in water to a yellow solution. It dissolves in HCl, and if the solution be treated with a reducing-agent (such as H_2S) it assumes a fine blue colour. If a solution of ammonium vanadate be mixed with tincture of galls, it gives an intensely black fluid, which forms an excellent ink, for it is not bleached by acids (which turn it blue), alkalies, or chlorine.

Vanadium has been obtained by heating its chloride in hydrogen, or by electrolysing a solution of an alkali vanadate in HCl, as a silver white metal (sp. gr. 5.5). It is not oxidised by air, and does not decompose water, but burns when strongly heated in air. Its melting-point is not known. It is insoluble in HCl, but soluble in HNO_3. Fused NaOH converts it into sodium vanadate.

The oxides of vanadium correspond in composition with those of nitrogen. VO is a basic oxide forming salts which give lavender-coloured solutions; these absorb oxygen rapidly from the air, and act as powerful reducing agents. V_2O_3 is a black crystalline body resembling plumbago, and capable of conducting electricity, obtained by heating vanadic anhydride in a current of hydrogen; it is insoluble in acids, and combines with bases to form *vanadites* (RVO_2). V_2O_4 is produced when V_2O_3 is heated in air; it dissolves in acids forming salts of vanadyl (VO), and in alkalies forming *hypovanadates* ($R_2V_4O_9$). Vanadic anhydride, V_2O_5, forms purple and green compounds with the above oxides. *Metavanadic acid*,

* *Vanadis*, a Scandinavian deity.

HVO_3, crystallises in beautiful golden scales. The yellow fuming liquid, formerly called chloride of vanadium, is really an oxychloride, *vanadyl trichloride*, $VOCl_3$. The oxychlorides, V_2O_2Cl, VOCl, and $VOCl_2$, have also been obtained. There are two compounds of vanadium with nitrogen, VN and VN_2. Ammonium meta-vanadate is now used as an oxygen-carrier for blacks in calico-printing, in conjunction with chlorates and aniline hydrochloride. The slag of the Creusot steel works is now the chief source of vanadic acid, of which it contains 2 per cent.

NIOBIUM,* Nb = 93.3, and TANTALUM, Ta = 181.6.

249*b*. These metals occur as *niobates* and *tantalates* respectively in several rare minerals, of which *columbite* from Massachusetts is most important. By fusing the mineral with $KHSO_4$, treating with water, digesting the insoluble residue with $(NH_4)_2S$ (to remove Sn and W), and with HCl to remove FeS, a mixture of Nb_2O_5 and Ta_2O_5 is obtained. This is dissolved in HF, and KHF_2 is added; on concentrating K_2TaF_7 crystallises first and is followed by $NbOF_3.2KF$; each yields the corresponding pentoxide when boiled with much water.

To extract Nb from Nb_2O_5 this is first converted into $NbCl_5$ (by ignition with charcoal and chlorine), the vapour of which is mixed with H and passed through a red-hot tube. The deposited metal is steel-grey (sp. gr. 7), burns to Nb_2O_5, and is insoluble in all acids except in a mixture of HF and HNO_3 and in H_2SO_4 conc.

By heating a mixture of Nb_2O_5 and C in the electric furnace a button of the metal is obtained, hard enough to scratch quartz. It melts above 1800° C.

Niobic anhydride, Nb_2O_5, is a white powder soluble in alkalies to form *meta-niobates*, $RNbO_3$. NbO and NbO_2 are also known. $NbCl_3$ and $NbCl_5$ have been prepared as well as oxychlorides analogous to those of vanadium.

A fused button of tantalum (containing 0.5 per cent. C.) may be obtained by heating a mixture of Ta_2O_5 and C in the electric furnace; it scratches quartz and has sp. gr. 12.79.

When heated at 600° C. in oxygen both niobium and tantalum burn to the pentoxide. They are both active reducing-agents at moderately high temperatures, niobium being the more active in this regard. Fused alkalies or nitre oxidise them to the corresponding metaniobate or metatantalate.

In its compounds tantalum resembles niobium.

The bismuth group of metals.—The metals Bi, Sb, Ta, Nb, and V belong to the same group of elements, which also includes N, P, and As. All these are characterised by their acid pentoxides. Ta, Nb, and V do not form hydrides analogous to PH_3, nor is BiH_3 known. Many points of resemblance may be noted between vanadium and chromium, whilst niobium and tantalum recall tungsten.

TIN.

Sn = 117.6 parts by weight.

250. Tin is by no means so widely diffused as most of the other metals which are largely used, and is scarcely ever found in the metallic state in nature. Its only important ore is that known as *tin-stone*, which is a binoxide of tin, SnO_2, and is generally found in veins traversing quartz, granite, or slate. It is generally associated with arsenical iron pyrites, and with a mineral called *wolfram*, which is a tungstate of iron and manganese.

Tin-stone is sometimes found in alluvial soils in the form of detached rounded masses; it is then called *stream tin ore*, and is much purer than that found in veins, for it has undergone a natural process of oxidation and levigation exactly similar to the artificial treatment of the impure ore. These detached masses of stream tin ore are not unfrequently rectangular prisms with pyramidal terminations.

* *Niobe*, daughter of *Tantalus*.

The Cornish mines, and those of Malacca and Banca, furnish the largest supplies of tin. Tin-stone is also found in Bohemia, Saxony, California, and Australia. At the Cornish tin-works the purer portions of the ore are picked out by hand, and the residue, which contains quartz and other earthy impurities, together with copper pyrites and arsenical iron pyrites, is reduced to a coarse powder in the stamping-mills, and washed in a stream of water. The tin-stone, being extremely hard, is not reduced to so fine a powder as the pyritic minerals associated with it, and these latter are therefore more readily carried away by the stream of water than is the tin-stone. The removal of the foreign matters from the ore is also much favoured by the high specific gravity of the binoxide of tin, which is 6.5, whilst that of sand or quartz is only 2.7, so that the latter would be carried off by a stream which would not disturb the former. So easily and completely can this separation be effected, that a sand containing less than 1 per cent. of tin-stone is found capable of being economically treated.

In order to expel any arsenic and sulphur which may still remain in the washed ore, it is roasted in quantities of 8 or 10 cwts. in a reverberatory furnace, when the sulphur is disengaged in the form of sulphurous acid gas, and the arsenic in that of arsenious oxide, the iron being left in the state of ferric oxide, and the copper partly as sulphate of copper, partly as unaltered sulphide. To complete the oxidation of the insoluble sulphide of copper, and its conversion into the soluble sulphate, the roasted ore is moistened with water and exposed to the air for some days, after which the whole of the copper may be removed by again washing with water.

A second washing in a stream of water also removes the ferric oxide in a state of suspension, and this is much more easily effected than when the iron was in the form of pyrites, since the difference between the specific gravity of this mineral (5.0) and that of the tin-stone (6.5) is far less than that between the sp. gr. of ferric oxide and tin-stone.

The ore thus purified contains between 60 and 70 per cent. of tin; it is mixed very intimately with about $\frac{1}{8}$th of powdered coal, and a little lime or fluor spar, to form a fusible slag with the siliceous impurities, and reduced in a reverberatory furnace, a comparatively easy task since binoxide of tin readily parts with its oxygen to carbon at a red heat.

The tin-smelting furnace is shown in Fig. 227. The mixture of ore and coal is moistened to prevent its dispersion by the draught of air, and spread on the hearth (A) in charges of between 20 and 25 cwts.

The temperature is not permitted to rise too high at first, lest a portion of the oxide of tin should combine with the silica to form a silicate, from which the metal would be reduced with difficulty. During the first six or eight hours the doors of the furnace are kept shut, so as to exclude the air and favour the reducing action of the carbon upon the binoxide of tin, the oxygen of which it converts into carbonic oxide, leaving the tin in the metallic state to accumulate upon the hearth beneath the layer of slag. When the reduction is deemed complete, the mass is well stirred with an iron paddle to separate the metal from the slag; the latter is run out first, and the tin is then drawn off into an iron pan (B), where it is allowed to remain at rest for the dross to rise to the surface, and is ladled out into ingot moulds.

The slags drawn out of the smelting-furnace are carefully sorted, those which contain much oxide of tin being worked up with the next charge of ore, whilst those in which globules of tin are disseminated are crushed, so that the metal may be separated by washing in a stream of water.

The tin, when first extracted from the ore, is far from pure, being contaminated

with small quantities of iron, arsenic, copper, and tungsten. In order to purify it from these, the metal is submitted to a process of *liquation*, in which the easy fusibility of tin is taken advantage of; the ingots are piled into a hollow heap near the fire-bridge of a reverberatory furnace, and gradually heated to the fusing-point, when the greater portion of the tin flows into an outer basin, whilst the remainder is converted into the binoxide, which remains as dross upon the hearth, together with the oxides of iron, copper, and tungsten, the arsenic having passed off in the form of arsenious oxide. Fresh ingots of tin are introduced at intervals, until about 5 tons of the metal have collected in the basin, which is commonly the case in about an hour after the commencement of the operation.

The specific gravity of tin being very low (7.285), any dross which may still remain mingled with it does not separate very readily; to obviate this, the molten metal is well agitated by stirring with wet wooden poles, or by lowering billets of wet wood into it, when the evolved bubbles of steam carry the impurities up to the surface in a kind of froth; the stirring is continued for about three hours, and the metal is allowed to remain at rest for two hours, when it is skimmed and ladled into ingot moulds (*block tin*). It is found that, in consequence of the lightness of the metal, and its tendency to separate from the other metals with which it is contaminated, the ingots which are cast from the metal first ladled out of the pot are purer than those from the bottom: this is shown by striking the hot ingots with a hammer, when they break up into the irregular prismatic fragments known as *dropped* or *grain tin*, the impure metal not exhibiting this extreme brittleness at a high temperature. The tin imported from Banca is celebrated for its purity (*Straits tin*).

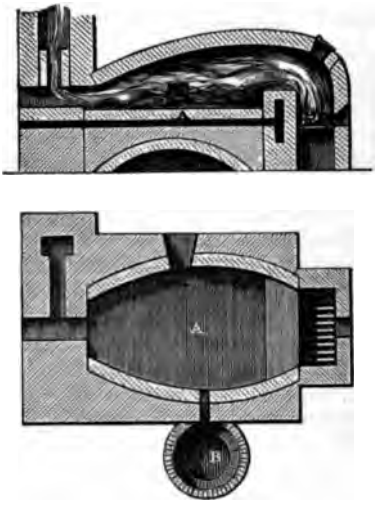


Fig. 227.

When the tin ore contains wolfram, $[FeMn]WO_4$, which has sp. gr. 7.3, this remains behind with the prepared tin ore, and must be removed before smelting by fusion with sodium carbonate in a reverberatory furnace, when the tungstic acid is converted into sodium tungstate, which is dissolved out by water, and crystallised. This salt finds an application in calico-printing.

On the small scale, tin may be extracted from tin-stone by fusing 100 grains with 20 grains of dried sodium carbonate, and 20 of dried borax, in a crucible lined with charcoal, exactly as in the extraction of iron (see p. 415).

The extraction is more easily effected by fusing 100 grains of tin-stone with 500 grains of potassium cyanide for fifteen minutes at a red heat.

251. **Properties of Tin.**—Tin is remarkable for its lustre and whiteness, in which it rivals silver, but is at once distinguished from the latter by its greater fusibility, and by its oxidising when heated in air. It is the most fusible of the metals in common use (233° C.), much lighter than silver, sp. gr. 7.28, and emits a curious grating sound when bent; it is harder than lead, but softer than zinc; very malleable at ordinary temperatures (*tin-foil*), brittle at 200° C. (*dropped* or *grain tin*), not vaporised except at very high temperatures. It has the lowest tenacity of all the metals in common use, and therefore its ductility is very low, only one other common metal, lead, being more difficult to draw into wire at the common temperature. Tin may, however, be drawn at 100° C. Only gold, silver, and copper surpass it in malleability.

Tin decomposes steam at a red heat. It is scarcely affected by air or

water at common temperatures,* and is therefore used for tinning other metals. Tin is easily soluble in strong hydrochloric acid, which distinguishes it from silver, and it is converted into a white nearly insoluble powder by nitric acid, which distinguishes it from all other metals except antimony.

Exposure to extreme cold converts tin into a modification which has lost its reflecting surface, and has thus acquired a grey appearance (*grey tin*). A spontaneous disintegration of the tin may even occur from this cause.† The sp. gr. of grey tin is 5.73.

The transition temperature of these enantiotropic forms of tin is 20° C., so that the grey form must become white when heated above this temperature; but the change from white to grey below 20° C. is very slow until the temperature has fallen considerably lower. The conversion is most rapid at −48° C., and is accelerated by contact with grey tin already formed, and with stannic chloride.

Tin-foil is made from bars of the best tin, which are hammered down to a certain thinness, then cut up, laid upon each other, and again beaten till extended to the required degree.

Tin-plate is made by coating sheets of iron with a layer of tin; to effect this, the sheets, cleansed from oxide, are dipped into melted tin, a coating of which adheres to the iron when the sheet is withdrawn. Tin being unaltered by exposure to air at the ordinary temperature, will effectually protect the iron from rust as long as the coating of tin is perfect, but as soon as a portion of the tin is removed so as to leave the iron exposed, corrosion occurs very rapidly, because the two metals form a galvanic couple, which decomposes the water (charged with carbonic acid) deposited upon them from the air, and the iron, having the greater attraction for oxygen, is the metal attacked. In the case of galvanised iron (coated with zinc), on the contrary, the zinc would be the metal attacked, and hence the greater durability of this material under certain conditions.

For the manufacture of tin-plate, the best mild steel is employed, and the most important part of the process consists in cleansing the iron plates from every trace of oxide which would prevent the adhesion of the tin. To effect this, and to anneal the iron, they are made to undergo several processes, of which the most important are—(1) immersion in diluted sulphuric acid; (2) heating to redness to anneal the plate; (3) rolling to improve the surface; (4) a second annealing; (5) immersion in diluted sulphuric acid; (6) scouring with sand; (7) washing with water; they are then dried for an hour in a vessel of melted tallow, which prevents contact of air, and immersed for an hour and a half in melted tin, the surface of which is protected from oxidation by tallow; after draining, they are dipped a second time into the tin to thicken the layer; then transferred to a bath of hot tallow to allow the superfluous tin to run down to the lower edge, whence it is afterwards removed by passing the plate through rollers. About 8 lbs. of tin are required to cover 225 plates, weighing 112 lbs.

To recover the tin from tin-plate cuttings they are boiled with caustic soda and litharge: $Sn + 2NaOH + 2PbO = Na_2SnO_3 + Pb_2 + H_2O$. The sodium stannate, Na_2SnO_3, is used in dye-works, and the precipitated lead is again converted into litharge by heating in air.

Terne-plate is iron coated with an alloy of tin and lead.

In tinning the interior of copper vessels, in order to prevent the contamination

* Crystalline tin (sp. gr. 7.18), deposited upon zinc from neutral stannous chloride, and powdered tin, made by shaking molten tin in a wooden box, oxidise to a considerable extent at the ordinary temperature; when heated, the superficial oxide prevents the tin from fusing, and it burns like tinder.

† The disintegration of the tin pipes of church organs, observed in cold climates, has been attributed to the conversion of the tin into the grey modification by the cold, perhaps aided by the vibrations to which the pipes are subjected.

of food with the copper, the surface is first thoroughly cleaned from oxide by heating it and rubbing over it a little sal-ammoniac, which decomposes any oxide of copper, converting it into the volatile chloride of copper ($CuO + 2NH_4Cl = CuCl_2 + H_2O + 2NH_3$). A little resin is then sprinkled upon the metallic surface, to protect it from oxidation, and the melted tin is spread over it with tow.

Pins (made of brass wire) are coated with tin by boiling them with cream of tartar (bitartrate of potash), common salt, alum, granulated tin, and water; the tin is dissolved by the acid liquid, from which solution it is reduced by electrolytic action, for the tin is more highly electro-positive than the brass, and the latter acts as the negative plate.

252. **Alloys.**—The term alloy is applied to any homogeneous mass consisting of two or more metals. In the majority of cases, it is not possible to detect the properties of the individual metals in such a mass, so that the alloy cannot be regarded as a mere mixture. In many cases, on the other hand, the alteration of properties induced in one metal by the addition of another does not show any definite relationship with the mass of the added metal, as would be the case if such alteration were wholly due to chemical combination. A little consideration will show that the difficulty thus experienced in assigning the phenomenon of alloy-formation to its proper position in the classes of change, usually distinguished as physical and chemical, is parallel to that experienced in assigning the phenomenon of solution to one of these two classes (p. 50). It has thus become customary to regard alloys as *solidified solutions*, which in some cases are analogous to what has been already termed a simple solution—that is, the alloy shows no evidence of containing a chemical compound—and in other cases are analogous to those solutions which undoubtedly contain a compound of the solvent with the dissolved substance in a state of simple solution. The majority of alloys belong to the second class, and consist of solutions of compounds of the constituent metals in an excess of one of the metals.

Two important pieces of evidence in favour of these views must be quoted. (1) In many instances, when one metal is alloyed, in small proportion, with another, the freezing-point of the preponderating metal is lowered to an extent which is in accord with the laws controlling the lowering of the freezing-point of a solvent by a dissolved solid (p. 319).* This indicates that the alloy is but a solidified solution. (2) When a compound plate (of copper and zinc, for instance), consisting of one metal closely attached to another, is used as the attackable plate of a galvanic cell, the electro-motive force of the cell is that which would be produced were the more attackable of these metals (zinc, for instance) alone used as the attackable plate. When an alloy is thus treated, the E.M.F. is in some cases that which would be produced by the more attackable constituent, and is in some cases different from this. Identity of the E.M.F. with that of the more attackable metal indicates that the alloy is a solidified simple solution, whereas a difference from this value can only be due to the existence of a compound in the alloy.

Alloys are industrially made by mixing the constituent metals in a melted condition, although they have been also prepared both by strongly compressing a mixture of the powdered metals at the ordinary temperature, and by electrolysing a solution containing salts of the constituent metals; the metallic deposit obtained by the latter method consists, in some cases, of an alloy.

252*a*. **Alloys of Tin.**—Tin is the chief metal used for making white alloys, some of which resemble silver in appearance. *Britannia metal* consists chiefly of tin (about 80 per cent.) hardened by antimony (about

* It may be remarked that evidence as to the molecular weight of metals has been obtained from alloys by a method analogous to that of Raoult (p. 319).

10 per cent.) and a little copper. Base silver coin consists chiefly of tin. *Pewter* consists of 4 parts of tin and 1 part of lead. Much inferior tin-foil is made of pewter. The fusibility of tin recommends it for *solder*. The solder employed for tin-wares is an alloy of tin and lead in various proportions, sometimes containing 2 parts of tin to 1 of lead (fine solder), sometimes equal weights of the two metals (common solder), and sometimes 2 parts of lead and 1 of tin (coarse solder). All these alloys melt at a lower temperature than tin, and, therefore, than lead. In applying solder, it is essential that the surfaces to be united be quite free from oxide, which would prevent adhesion of the solder; this is insured by the application of sal ammoniac, or of hydrochloric acid,* or sometimes of powdered borax, remarkable for its ready fusibility and its solvent power for the metallic oxides.

Gun metal is an alloy of 90.5 parts of copper with 9.5 of tin, especially valuable for its tenacity, hardness, and fusibility.

In preparing this alloy, it is usual to melt the tin in the first place with twice its weight of copper, when a white, hard, and extremely brittle alloy (*hard metal*) is obtained. The remainder of the copper is fused in a de-oxidising flame on the hearth of a reverberatory furnace, and the hard metal thoroughly mixed with it, long wooden stirrers being employed. A quantity of old gun metal is usually melted with the copper, and facilitates the mixing of the metals. When the metals are thoroughly mixed, the oxide is removed from the surface and the gun-metal is run into moulds made of loam, the stirring being continued during the running, in order to prevent the separation, to which this alloy is very liable, of a white alloy containing a larger proportion of tin, which has a lower specific gravity, and would chiefly collect in the upper part of the casting (forming *tin-spots*). The purest commercial qualities of copper and tin are always employed in gun-metal.

The brittle white alloy alluded to above as *hard metal* appears to be a chemical compound having the formula $SnCu_4$ (which requires 31.8 per cent. of tin and 68.2 per cent. of copper), though the alloy which has the highest density, and bears repeated fusion without alteration in its composition, corresponds with the formula $SnCu_3$ (38.2 per cent. of tin). It is probably one of these alloys which forms the tin-spots or flaws in gun-metal castings.

Bronze is essentially an alloy of copper and tin, containing more tin than gun-metal contains; its composition is varied according to its application, small quantities of zinc and lead being often added to it. Bronze is affected by changes of temperature, in a manner precisely the reverse of that in which steel is influenced, for it becomes hard and brittle when allowed to cool slowly, but soft and malleable when quickly cooled, a property which the ancients applied in the manufacture of weapons. *Bronze coin* (substituted for the copper coinage) is composed of 95 copper, 4 tin, and 1 zinc. *Manganese-bronze*, an alloy of ordinary bronze containing Mn, is said to rival bar-iron in tenacity and extensibility; it is used for ships' propellers. *Phosphor-bronze* contains about $\frac{1}{2}$ per cent. of phosphorus added as tin phosphide.

Bell-metal is an alloy of about 4 parts of copper and 1 of tin, to which lead and zinc are sometimes added. The metal of which musical instruments are made generally contains the same proportions of copper and tin as bell-metal. At a little below a dark red heat, this alloy may be hammered into thin plates, imitating the celebrated Chinese gongs.

Speculum metal, employed for reflectors in optical instruments, consists of 2 parts of copper and 1 of tin, to which a little Zn, As, and Ag are sometimes added to harden it and render it susceptible to a high

* It is customary to *kill* the hydrochloric acid by dissolving some zinc in it. The chloride of zinc is probably useful in protecting the work from oxidation.

polish. A superior kind of *type-metal* is composed of 1 part of Sn, 1 of Sb, and 2 of Pb.

Tin is not dissolved by nitric acid, but is converted into a white powder, *metastannic acid;* hydrochloric acid dissolves it with the aid of heat, evolving hydrogen; but the best solvent for tin is a mixture of hydrochloric with a little nitric acid. When the metal is acted upon by hydrochloric acid, it assumes a crystalline appearance, which has been turned to account for ornamenting tin-plate. If a piece of common tin-plate be rubbed over with tow dipped in a warm mixture of hydrochloric and nitric acids, its surface is very prettily diversified (*moiré métallique*); it is usual to cover the surface with a coloured transparent varnish.

A mixture of 1 vol. H_2SO_4, 2 vols. HNO_3, and 3 vols. water dissolves tin in the cold, evolving nearly pure nitrous oxide. The solution is precipitated when heated. Poured into boiling water, all the tin is thrown down as metastannic acid.

Commercial tin is liable to contain minute quantities of lead, iron, copper, arsenic, antimony, bismuth, gold, molybdenum, and tungsten. Pure tin may be precipitated in crystals by the feeble galvanic current excited by immersing a plate of tin in a strong solution of stannous chloride, covered with a layer of water, so that the metal may be in contact with both layers of liquid.

253. **Oxides of tin.**—Two oxides of this metal are known—stannous oxide, SnO, and stannic oxide, SnO_2.

Protoxide of tin (SnO), or *stannous oxide*, is a substance of little practical importance, obtained by heating stannous oxalate out of contact with air; $SnC_2O_4 = SnO + CO_2 + CO$. It is a black powder which burns when heated in air, becoming SnO_2. It is a feebly basic oxide, and therefore dissolves in the acids; it may also be dissolved by a strong solution of potash, but is then easily decomposed into metallic tin and stannic oxide, which combines with the potash. By heating tin with caustic soda a "*stannite*" of soda is obtained; this is substituted for stannate of soda, into which it is converted, with precipitation of tin, by boiling.

Binoxide of tin (SnO_2) or *stannic oxide*, has been mentioned as the chief ore of tin, and is formed when tin is heated in air. *Tin-stone*, or *cassiterite*, as the natural form of this oxide is called, occurs in very hard square prisms, usually coloured brown by ferric oxide. In its insolubility in acids it resembles crystallised silica, and, like that substance, it forms, when fused with alkalies or their carbonates, compounds which are soluble in water; these are termed *stannates*, the binoxide of tin being known as *stannic anhydride*. The artificial SnO_2 dissolves in hot strong H_2SO_4, and is precipitated on adding water. It is easily reduced when heated in hydrogen, and is converted into $SnCl_4$ when heated in HCl gas.

Sodium stannate, $Na_2O.SnO_2$, is prepared, on the large scale, for use as a mordant by calico-printers. The prepared tin ore (p. 448) is heated with solution of caustic soda, and boiled down till the temperature rises to 600° F. (315° C.); or the tin ore is fused with sodium nitrate, when the nitric acid is expelled. It crystallises easily in hexagonal tables having the composition $Na_2SnO_3.3Aq$, which dissolve easily in cold water, and are partly deposited again when the solution is heated. Prismatic crystals have been obtained of $Na_2SnO_3.10Aq$, like $Na_2CO_3.10Aq$. Most normal salts of the alkalies also cause a

separation of sodium stannate from its aqueous solution. The solution of sodium stannate has, like the silicate, a strong alkaline reaction, and when neutralised by an acid yields a precipitate of stannic acid, H_2SnO_3, or $SnO(OH)_2$, which may be obtained as a hydrosol and a hydrogel exactly as described for silicic acid (p. 278). The great similarity between stannic and silicic acids is here very remarkable. When heated, stannic acid is converted into SnO_2.

Stannic or *metastannic acid*, H_2SnO_3 (dried at 100° C.), is obtained as a white crystalline hydrate when tin is oxidised by nitric acid. When heated, it assumes a yellowish colour, and a hardness resembling that of powdered tin-stone. *Putty powder*, used for polishing, consists of metastannic anhydride: as found in commerce, it generally contains much oxide of lead. Metastannic acid is insoluble in water and diluted acids, but when boiled with dilute HCl it combines with some of the acid, and when the excess of HCl has been removed by washing, the compound passes into solution, from which it is reprecipitated by HCl, or by boiling. When *fused* with hydrated alkalies it is converted into a soluble stannate, but if *boiled* with solution of potash it is dissolved in the form of potassium metastannate, which will not crystallise, like the stannate, but is obtained as a granular precipitate by dissolving potassium hydrate in its solution. This precipitate has the composition $K_2Sn_5O_{11}.4Aq$; it is very soluble in water, and is strongly alkaline. When it is heated to expel the water, it is decomposed, and the potash may be washed out with water, leaving metastannic anhydride. The *sodium metastannate*, $Na_2Sn_5O_{11}.4Aq$, has also been obtained as a sparingly soluble crystalline powder, by the action of cold sodium hydroxide on metastannic acid. It is claimed that the precipitate formed by alkalies in stannic chloride is orthostannic acid, $Sn(OH)_4$.

Stannate of tin is obtained as a yellowish hydrate by boiling stannous chloride with ferric hydroxide; $Fe_2O_3 + 2SnCl_2 = SnSnO_3 + 2FeCl_2$. It is sometimes written Sn_2O_3, and called *sesquioxide of tin*.

Stannous nitrate, $Sn(NO_3)_2$, is formed when tin is dissolved in cold very dilute nitric acid; $Sn_4 + 10HNO_3 = 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O$. It forms a yellow solution, which absorbs oxygen and deposits SnO_2. *Stannic nitrate*, $Sn(NO_3)_4$, has been crystallised from a solution of stannic acid in nitric acid.

254. **Chlorides of tin.**—The two chlorides of tin correspond in composition with the oxides.

Stannous chloride, or *protochloride of tin* ($SnCl_2$), is much used by dyers and calico-printers,* and is prepared by dissolving tin in hydrochloric acid, when it is deposited, on cooling, in lustrous prismatic needles ($SnCl_2.2Aq$) known as *tin crystals* or *salts of tin*. *In vacuo*, over H_2SO_4, they become $SnCl_2$ (m. p. 249° C.). The dissolution of the tin is generally effected in a copper vessel, in order to accelerate the action by forming a voltaic couple, of which the tin is the attacked metal. When gently heated, the crystals lose their water, and are partly decomposed, some hydrochloric acid being evolved ($SnCl_2 + H_2O = SnO + 2HCl$); at a higher temperature (610° C.) the anhydrous chloride may be distilled. The crystallised stannous chloride dissolves in about one-third of its weight of water, but if much water be added, a precipitate of *stannous hydroxychloride*, $2Sn(OH)Cl.Aq$, is formed, which dissolves on adding HCl. A moderately dilute solution of stannous chloride absorbs oxygen from the air, and deposits the hydroxychloride, leaving stannic chloride in solution; $3SnCl_2 + H_2O + O = SnCl_4 + 2Sn(OH)Cl$. If the solution contains much free hydrochloric acid, it remains clear, being entirely converted into stannic chloride. A strong solution of the chloride is not oxidised by the air, and the weak solution may be longer preserved in contact with metallic tin. Stannous chloride has a great attraction

* It is sometimes used for imparting a fine golden colour to sugar.

for chlorine as well as for oxygen, and is frequently employed as a de-oxidising or de-chlorinating agent. Tin may be precipitated from stannous chloride by the action of zinc, in the form of minute crystals. A very beautiful *tin tree* is obtained by dissolving granulated tin in strong hydrochloric acid, with the aid of heat, in the proportion of 8 measured oz. of acid to 1000 grs. of tin, diluting the solution with four times its bulk of water, and introducing a piece of zinc.

Stannous chloride is also obtained by heating tin in HCl gas, or by distilling tin with mercuric chloride; $Sn + HgCl_2 = SnCl_2 + Hg$. The mercury distils over, leaving the stannous chloride as a transparent vitreous mass. Above 880° C. the density of its vapour is 94.5 (H = 1), agreeing with the formula $SnCl_2$, but below 700° C. it is 189, corresponding with Sn_2Cl_4.

Stannic chloride or *tetrachloride of tin* ($SnCl_4$), is obtained in solution when tin is heated with hydrochloric and nitric acids; for the use of the dyer, the solution (*nitromuriate of tin*) is generally made with chloride of ammonium (sal-ammoniac) and nitric acid. The anhydrous tetrachloride is obtained by heating tin in a current of dry chlorine, when combination occurs with combustion, and the tetrachloride distils over as a heavy (sp. gr. 2.28) colourless volatile liquid (boiling-point, 114° C.), giving suffocating white fumes in the air. When it is mixed with a little water, there is energetic combination, and three crystalline compounds may be produced, containing 3, 5, and 8 molecules of water. A large quantity of water causes precipitation of stannic acid. The commercial crystals are $SnCl_4.5Aq$. The anhydrous chloride is also obtained by distilling tin with an excess of mercuric chloride; $Sn + 2HgCl_2 = SnCl_4 + Hg_2$; but here, the result is opposite to that in the case of stannous chloride, as the stannic chloride distils over before the mercury. Stannic chloride forms crystallisable double salts with the alkali chlorides. *Pink salt*, used by dyers, is a compound of stannic chloride with ammonium chloride, $2NH_4Cl.SnCl_4$; it is colourless, but is used in dying red with madder. The compound $2HCl.SnCl_4.6Aq$ has been obtained in crystals.

Stannic bromide, $SnBr_4$, is crystalline, fuses at 30° C., and boils at 201° C. It dissolves in water without immediate decomposition.

255. **Sulphides of tin.**—The *protosulphide*, or *stannous sulphide* (SnS), may be easily prepared by heating tin with sulphur, when it forms a grey crystalline mass. It is also obtained as a dark brown precipitate by the action of H_2S upon a solution of $SnCl_2$. Stannous sulphide is not dissolved by alkalies unless some sulphur be added, which converts it into stannic sulphide. It dissolves in hot strong HCl.

Bisulphide of tin, or *stannic sulphide* (SnS_2), is commonly known as *mosaic gold* or *bronze powder*,* and is used for decorative purposes. It cannot be made by heating tin with sulphur, because it is decomposed by heat into SnS and S. It is prepared by a curious process, which was devised in 1771, and must have been the result of a number of trials. 12 parts by weight of tin are dissolved in 6 parts of mercury; the brittle amalgam thus obtained is powdered and mixed with 7 parts of sulphur and 6 of sal-ammoniac. The mixture is introduced into a

* A *bronze powder* is also made by powdering finely laminated alloys of copper and zinc a little oil being used to prevent oxidation.

Florence flask, which is gently heated in a sand-bath as long as any smell of H_2S is evolved; the temperature is then raised to dull redness until no more fumes are disengaged. The mosaic gold is found in beautiful yellow scales at the bottom of the flask, and sulphide of mercury and calomel are deposited in the neck. The mercury appears to be used for effecting the fine division of the tin, and the sal-ammoniac to keep down the temperature (by its volatilisation) below the point at which the SnS_2 is converted into SnS.

Mosaic gold, like gold itself, is not dissolved by hydrochloric or nitric acid, but easily by *aqua regia*. Alkalies also dissolve it when heated. On adding H_2S to a solution of stannic chloride, the stannic sulphide is obtained as a yellow precipitate, which is sometimes formed only on boiling. It dissolves easily in alkalies and alkali sulphides, forming *thiostannates*. The sodium salt, $Na_2SnS_3.2H_2O$, has been crystallised in yellow octahedra. When fused with iodine, SnS_2 forms SnS_2I_4, a fusible yellow body which does not lose iodine when heated, and dissolves in carbon disulphide, forming a brown solution which deposits red crystals like potassium dichromate; these are decomposed by boiling with water, yielding SnO_2, sulphur, iodine, and HI.

Tin pyrites contains either SnS or SnS_2, or both, accompanied by sulphides of copper and iron.

Stannic sulphate, $Sn(SO_4)_2$, is left as a white mass when tin is boiled to dryness with sulphuric acid.

Stannic phosphate, $Sn_3(PO_4)_4$, is insoluble in nitric acid, and is sometimes used in separating phosphoric acid in quantitative analysis.

Stannic arsenate is left in the residue obtained by oxidising alloys containing tin and arsenic with nitric acid.

Tin is very closely connected with silicon by the composition, hardness, and insolubility of SnO_2, and by the characters of $SnCl_4$. Among metals it is conspicuous by the feebly basic character of its oxides and by the powerful reducing properties of $SnCl_2$.

TITANIUM, Ti = 47.7.

256. This metal stands in close chemical relationship to tin: it is found in considerable quantity in iron ores and clays, although no very important practical application has hitherto been found for it. The form in which it is generally found is *titanic oxide* (or *anhydride*), TiO_2, which occurs uncombined in the minerals *rutile*, *anatase*, and *brookite*, the first of which is isomorphous with tin-stone, and is extremely hard, like that mineral, while the second crystallises in the quadratic system and the third in the rhombic. The mineral *perowskite* is $(CaFe)TiO_3$. In combination with oxide of iron, titanic oxide is found in *iron-sand*, *iserine*, or *menaccanite* (found originally in Menaccan, in Cornwall), which resembles gunpowder in appearance, and is now imported in abundance from Nova Scotia and New Zealand. Some specimens of this mineral contain 40 per cent. of titanic oxide as ferrous titanate. To extract titanic oxide from it, the finely ground mineral is fused with three parts of K_2CO_3, when CO_2 is expelled and potassium titanate (K_2TiO_3) formed; on washing the mass with hot water, this salt is decomposed, a part of its alkali being removed by the water, and an acid titanate left, mixed with the oxide of iron. This is dissolved in HCl, and the solution evaporated to dryness, when the titanic oxide, and any silica which may be present, are converted into the insoluble modifications, and are left on digesting the residue again with dilute hydrochloric acid; the residue is washed with water (by decantation, for titanic oxide easily passes through the filter), dried, and fused at a gentle heat with $KHSO_4$. This forms a soluble compound with the titanic oxide, which may be extracted by cold water, leaving the silica undissolved. The solution containing the titanic oxide is mixed with about twenty times its volume of water, and boiled for some time, when the TiO_2 is separated as a white precipitate, exhibiting a great disposition to cling as a film to the surface of the flask in which the solution is boiled, and giving it the appearance of being corroded. The titanic oxide becomes yellow when strongly heated, and white again on cooling; it does not dissolve in solution of potash, like silica, but when fused with

potash it forms a titanate, which is decomposed by water; the acid titanate of potassium which is left may be dissolved in HCl, and if the solution be neutralised with ammonium carbonate, hydrated titanic acid, $Ti(OH)_4$, is precipitated, very much resembling alumina in appearance. By dissolving the gelatinous hydrate in cold HCl, and dialysing, a solution of titanic acid in water is obtained, which is liable to gelatinise spontaneously if it contains more than 1 per cent. of the acid. Titanic acid is employed in the manufacture of artificial teeth, and for imparting a straw-yellow tint to the glaze of porcelain.

If a mixture of titanic acid and charcoal be heated to redness in a porcelain tube through which dry chlorine is passed, *titanium tetrachloride* ($TiCl_4$) is obtained as a colourless volatile liquid (b. p. 136° C.), very similar to tetrachloride of tin. By passing the vapour of the tetrachloride over heated sodium, the *metallic titanium* is obtained in prismatic crystals (sp. gr. 3.6) resembling specular iron ore in appearance; it fuses at a very high temperature, but can be prepared massive by heating a mixture of TiO_2 and C in the electric furnace, when it contains about 2 per cent. of carbon, is hard enough to scratch rock crystal and has sp. gr. 4.87. Like tin, it is said to dissolve in hydrochloric acid with liberation of hydrogen. The most remarkable chemical feature of titanium is its direct attraction for nitrogen, with which it combines when strongly heated in air. By passing ammonia gas over titanic oxide heated to redness, a yellow powder is formed, which is nitride of titanium (Ti_2N_2). When suspended in water, it is blue by transmitted and yellow by reflected light. Ti_3N_4, corresponding with $TiCl_4$, is also known. Beautiful cubes of a copper colour and great hardness, formerly believed to be metallic titanium, are found adhering to the slags of blast furnaces in which titaniferous iron ores are smelted; these are believed to consist of a compound of cyanide with nitride of titanium, $TiCy_2.3Ti_3N_2$. A similar compound is obtained by passing nitrogen over a mixture of titanic oxide and charcoal heated to whiteness.

Violet-coloured crystals of *titanium trichloride* (Ti_2Cl_6) are obtained by passing hydrogen charged with vapour of the tetrachloride through a red-hot porcelain tube; it forms a violet solution in water, which resembles stannous chloride in its reducing properties.

Titanium dichloride, $TiCl_2$, is obtained by heating the trichloride to dull redness in hydrogen. It is a black solid which quickly absorbs moisture, and takes fire if water be dropped upon it. When dissolved in water or alcohol, it evolves hydrogen from them. Bromine combines with it, causing much heat, and forming $TiCl_2Br_2$. The dichloride volatilises in hydrogen without fusing, and if cooled in hydrogen it occludes the gas, and takes fire on exposure to air. It glows when heated on platinum, evolving $TiCl_4$, and leaving a residue of TiO_2.

Titanium tetrafluoride, TiF_4 is prepared like SiF_4, and is a fuming colourless liquid. The *fluotitanates*, *e.g.*, K_2TiF_6, are prepared by dissolving TiO_2 in HF and neutralising with alkali.

When a solution of titanic oxide (or acid titanate of potassium) in hydrochloric acid is acted on by zinc, a violet solution is formed, which deposits, after a time, a blue (or green) precipitate; this appears to be a *sesquioxide of titanium* (Ti_2O_3), and rapidly absorbs oxygen from the air, being converted into titanic oxide. This oxide is also obtained in the preparation of $TiCl_2$ unless air be very carefully excluded. It then forms small shining copper-coloured crystals with a violet reflection, which have the same crystalline form as specular iron ore (Fe_2O_3). Ti_2O_3 is a basic oxide. The sulphate $Ti_2(SO_4)_3.8Aq$ crystallises from the violet solution obtained by dissolving titanium in sulphuric acid. Nitric acid oxidises it to *titanic sulphate*, $Ti(SO_4)_2.3Aq$, which forms a yellowish, transparent, deliquescent mass. Thus, TiO_2 appears to possess feebly basic as well as feebly acid properties. The *potassio-titanic sulphate*, $K_2Ti(SO_4)_3.3Aq$. is formed when TiO_2 is fused with $KHSO_4$. A *titanous oxide* (TiO) is said to be obtained as a black powder when titanic oxide is strongly heated in a crucible lined with charcoal.

Titanium trioxide TiO_3, is obtained as a yellow precipitate, $Ti(OH)_6$, when $TiCl_4$ is mixed with a dilute solution of H_2O_2 in alcohol. It is probably a peroxide, and is the cause of the yellow colour developed by H_2O_2 in solution of titanic acid forming a test for H_2O_2 (p. 64).

Titanium disulphide is not precipitated, like tin disulphide when H_2S acts upon the tetrachloride; but if a mixture of the vapour of titanium tetrachloride with hydrosulphuric acid is passed through a red-hot tube, greenish-yellow scales of the disulphide, resembling mosaic gold, are deposited.

ZIRCONIUM, Zr = 90.

257. This metal occurs in the rare minerals *zircon* (sp. gr. 4.5) and *hyacinth*, in which the oxide *zirconia* (ZrO_2) is combined with silica ($ZrO_2.SiO_2$). The ZrO_2 is obtained from these minerals by heating with KHF_2, and boiling with water when K_2SiF_6 is left and K_2ZrF_6 dissolved; this is heated with H_2SO_4 to expel HF, and $ZrO(OH)_2$ is precipitated by ammonia: when this is ignited, it incandesces, loses water, and becomes ZrO_2, which is a feebly acid oxide, liberating CO_2 from fused Na_2CO_3, and forming *sodium zirconate*, Na_4ZrO_4.

Zr closely resembles Si, and is obtained like that element; it exists in an amorphous and a crystalline (sp. gr. 4.25) form. It dissolves in HF and in *aqua regia* and decomposes water slowly at 100° C. Its melting-point is very high. Zinconia is more basic than silica, and the metal displaces silicon when heated with silica. The sulphate, $Zr(SO_4)_2.4Aq$, is decomposed by boiling with K_2SO_4, recalling the behaviour of titanium. $ZrCl_4$ is known; it is more stable than $SiCl_4$. Evidence of the existence of higher oxides than ZrO_2 has been obtained.

THORIUM, $Th^{IV} = 230.8$.

Although a rare element, thorium in the form of *thoria*, ThO_2 (sp. gr. 10.2), is used in considerable quantity for the manufacture of Welsbach mantles (p. 155). The mineral *thorite*, $ThO_2.SiO_2$, is the most fruitful source of thoria but it is rare, and the oxide is commonly produced from *monazite sand*, which is comparatively poor in thorium, by fusion with caustic alkali, extraction with sulphurous acid and evaporation of the residue with strong H_2SO_4; the dry mass is added in small doses to water at 0° C. in which anhydrous thorium sulphate is readily soluble. Sodium sulphate is next added to precipitate cerium and *thorium hydroxide*, $Th(OH)_4$, is then thrown down by some substance acting as a feeble base, like sodium nitrite. Thoria is more basic than ZrO_2 but less acid, as it does not expel CO_2 from fused Na_2CO_3. Its anhydrous *sulphate*, $Th(SO_4)_2$, is soluble in ice-cold water, but when the solution is heated crystals of $Th(SO_4)_2.4H_2O$ separate. Thoria does not dissolve in HCl or HNO_3, but when the acid is expelled on the steam bath, the residue dissolves in the water to an emulsion in which acids cause a curdy precipitate soluble in pure water (compare metastannic acid). NH_3 produces a bulky precipitate of hydroxide which dissolves in cold nitric acid yielding the *nitrate* $Th(NO_3)_4.6H_2O$. *Thorium fluoride* is a precipitate insoluble in HF; the double fluoride $K_2ThF_6.4H_2O$ is a sparingly soluble crystalline powder.

Thorium prepared by dissolving the hydroxide in HCl, evaporating with KCl, and fusing the double chloride with sodium, is a grey crystalline metal isomorphous with silicon, of sp. gr. 11.1. It is very infusible, burns in air below a red heat, dissolves in dilute acids, and does not decompose water.

The radio-activity of thorium compounds has already been noticed (p. 438).

GERMANIUM, Ge = 71.5.

258. This occurs in *argyrodite*, a silver ore. It is extracted by fusing the powdered mineral with Na_2CO_3 and S, extracting with water, neutralising the solution with H_2SO_4, filtering from the precipitated S, As_2S_3, and Sb_2S_3, and saturating with H_2S, which precipitates white *germanic sulphide*, GeS_2. This is roasted to oxide, from which the metal is reduced by heating with H or C. It is a white brittle metal (sp. gr. 5.47), melts about 900° C., and volatilises at higher temperatures; the fused metal crystallises in octahedra. It is dissolved by H_2SO_4, but not by HCl; HNO_3 oxidises it to GeO_2.

Germanium stands between silicon and tin in the periodic table (p. 302), but it is more nearly related to tin than to silicon; its existence was prophesied (*ekasilicon*) by Mendeléeff previously to its discovery (1885). It is believed to form two classes of salts, corresponding with oxides GeO and GeO_2, respectively. The only *germanous salt*, which is authentically known, however, is the sulphide GeS. *Germanic chloride*, $GeCl_4$, is obtained like stannic chloride and boils at 86° C. When Ge is heated in HCl it yields *germanium chloroform*, $GeHCl_3$, which boils at 72° C. It is doubtful whether $GeCl_2$ exists. GeO_2 dissolves in HF and the solution yields double fluorides like K_2GeF_6, similar to the silico-fluorides.

Germanic oxide, GeO_2, is white, and sparingly soluble in water, from which it may be crystallised; it functions as an acid oxide.

GeS_2 is a white precipitate obtained by adding H_2S to a solution of GeO_2 in

HCl or H_2SO_4. In the absence of acid it is somewhat soluble in water. It is dissolved by alkali sulphides. When reduced by hot H it yields GeS in dark grey lustrous crystals, decomposed by potash into GeS_2, which dissolves, and Ge which separates.

CERIUM, Ce = 139.

259. This element is now classed with those related to tin, but in many respects it resembles those of the aluminium group. It occurs chiefly in *cerite*, which is essentially a silicate of the metal containing about 60 per cent. of Ce_2O_3. This oxide, *ceria*, is obtained for the manufacture of Welsbach mantles (p. 155) from monazite sand, as has been described under thorium.

The metal is prepared by electrolysing fused *cerous chloride* $CeCl_6$, itself obtained by evaporating Ce_2O_3 with HCl and NH_4Cl and igniting. Cerium is a grey, lustrous, malleable, ductile metal, unchanged by dry air, but becoming iridescent in moist air; its sp. gr. is 6.7 and it melts about 700° C. It burns in air more easily than magnesium does, and with a brighter light; it is soluble in dilute acid, and decomposes water slowly.

Three oxides, *cerous oxide*, Ce_2O_3, *ceric oxide*, CeO_2, and a *peroxide*, CeO_3, are known. The first is obtained by igniting the oxalate in hydrogen. It is grey, and rapidly oxidises to the pale yellow CeO_2, which is easily reduced again to Ce_2O_3; thus when it is boiled with HCl it liberates Cl and dissolves as Ce_2Cl_6. The peroxide is a reddish yellow precipitate formed on adding NH_3 and H_2O_2 to a solution of a cerous salt.

Ce_2O_3 is a stronger base than CeO_2 which, however, has no acid properties. The *cerous salts* (corresponding with Ce_2O_3) are colourless and more stable than the ceric salts (corresponding with CeO_2), which are yellow or red, and are easily reduced to cerous salts. No ceric chloride is known, but the *fluoride*, $CeF_4.H_2O$, yielding the double fluoride $2CeF_4.3KF.2H_2O$, has been obtained.

LEAD.

Pb″ = 205.4 parts by weight.

260. Lead owes its usefulness in the metallic state chiefly to its softness and fusibility. The former quality allows it to be easily rolled into thin sheets and to be drawn into the form of tubes or pipes; it is indeed the softest of the metals in common use, and at the same time the least tenacious, so that it can only be drawn with difficulty into thin wire, and is then very easily broken. The ease with which it makes a dark streak upon paper shows how readily minute particles of the metal may be abraded. Its want of elasticity also recommends it for some special uses, as for deadening a shock or preventing a rebound.

In fusibility it surpasses all the other metals commonly employed in the metallic state, except tin, for it melts at 617° F. (325° C.), and this circumstance, taken in conjunction with its high specific gravity (11.4), particularly adapts it for the manufacture of shot and bullets. For one of its extensive uses, however, as a covering for roofs, it would be better suited if it were lighter and less fusible, for in case of fire in houses so roofed, the fall of the molten lead frequently aggravates the calamity. Its resistance to strong acids is turned to account in manufacturing chemistry.

With the exception, perhaps, of the ores of iron, none is more abundant in this country than the chief ore of lead, *galena*, a sulphide of lead (PbS). This ore might at the first glance be mistaken for the metal itself, from its high specific gravity (7.5) and metallic lustre. It is found forming extensive veins in Cumberland, Derbyshire, and Cornwall, traversing a limestone rock in the first two counties, and a clay slate in the last. Spain also furnishes large supplies of this important ore. Galena

presents a beautiful crystalline appearance, being often found in large isolated cubes, which readily cleave or split up in directions parallel to their faces. Blende (sulphide of zinc) and copper pyrites (sulphide of copper and iron) are frequently found in the same vein with galena, and it is usually associated with quartz (silica), heavy spar (barium sulphate), or fluor spar (calcium fluoride). Considerable quantities of sulphide of silver are often present in galena, and in many specimens the sulphides of bismuth and antimony are found.

Though the sulphide is the most abundant natural combination of lead, it is by no means the only form in which this metal is found. The metal itself is occasionally met with, though in very small quantity, and the carbonate of lead ($PbCO_3$), *white lead ore* or *cerussite*, forms an important ore in the United States and in Spain. The sulphate of lead, *anglesite* ($PbSO_4$), is also found in Australia, and is largely imported into this country to be smelted.

261. The extraction of lead from galena is effected by one of three methods, the first of which is the oldest, and is still employed in the Flintshire works.

(1) Advantage is taken of the circumstance that, in the case of many metals, when a combination of the metal with oxygen is raised to a high temperature in contact with a sulphide of the same metal, the oxygen and sulphur unite, and the metal is liberated (*self-reduction*), thus, $PbS + 2PbO = Pb_3 + SO_2$. Since galena, when heated with free access of air, becomes to a great extent oxidised to PbO, it will be apparent that the necessary mixture of oxide and sulphide can be obtained by roasting the galena for a certain time, namely, until two-thirds of the lead has become oxide. This change cannot be brought about, however, without the simultaneous oxidation of some of the PbS into lead sulphate ($PbSO_4$); fortunately, this is of no consequence, since PbS and $PbSO_4$ react with each other at a high temperature, in accordance with the equation, $PbSO_4 + PbS = Pb_2 + 2SO_2$.

It will now be understood that the essential operations in this metallurgical process consist in roasting the ore (PbS) in presence of air until a sufficient proportion of it has been oxidised, and in then raising the temperature in order that the mixture of PbS, PbO, and $PbSO_4$, produced by the roasting, may react in the sense of the above equations.

The ore, having been separated by mechanical treatment, as far as possible, from the foreign matters associated with it, is mixed with a small proportion of lime to flux the siliceous matter of the ore, and spread over the hearth of a reverberatory furnace (Fig. 228), the sides of which are considerably inclined towards the centre, so as to form a hollow for the reception of the molten lead.

During the first or roasting stage of the smelting process the temperature is kept below that at which galena fuses. The ore is stirred from time to time, to expose fresh surfaces to the action of the atmospheric oxygen. When the roasting is sufficiently advanced, some fuel is thrown into the grate, the damper is slightly raised, and the doors of the furnace are closed, so that the charge may be heated to the temperature at which the oxide and sulphate of lead act upon the unaltered sulphide, furnishing metallic lead.

During this part of the operation the contents of the hearth are constantly raked up towards the fire-bridge, so as to facilitate the separation of the lead, and to cause it to run down into the hollow provided for its reception. It is also found that the separation of the lead from the slags is much assisted by occasionally throwing open the doors to chill the furnace. After about four hours the charge is reduced to a pretty fluid condition, the lead having accumulated at the bottom of the depressed portion of the hearth with the slag above it; this slag consists chiefly

of the silicates of lime and of oxide of lead, and would have contained a larger proportion of the latter if the lime had not been added as a flux at the commencement of the operation. In order still further to reduce the quantity of lead in the slag, a few more shovelfuls of lime are now thrown into the hearth, together with a little small coal, the latter serving to reduce to the metallic state the oxide of lead displaced by the lime from its combination with the silica. But since silicate of lime is far less fusible than silicate of lead, the effect of this addition of lime is to dry up the slags to a semi-solid mass, and it will now be seen that if the whole of the lime had been added at the commencement of the smelting, the diminished fusibility of the slag would have opposed an obstacle to the separation of the metallic lead.

During the last hour or so the temperature is very considerably raised, and at the expiration of about six hours, when the greater portion of the lead is thought to have separated, the slag is raked out through one of the doors of the furnace, and the melted metal allowed to run out through a tap-hole in front of the lowest portion of the hearth into an iron basin, from which it is ladled into pig-moulds. The rich slags are worked up again with a fresh charge of ore.

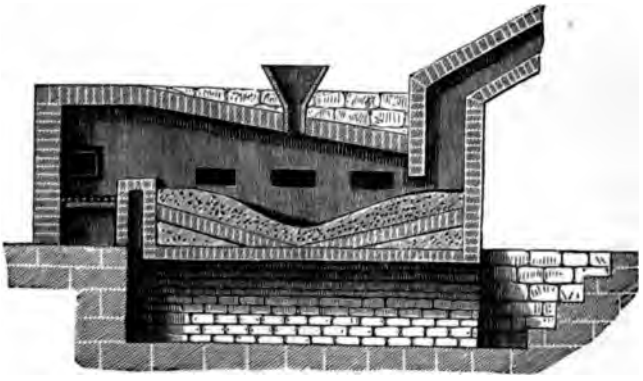


Fig. 228.—Furnace for smelting lead ores.

In the smelting of galena a very considerable quantity of lead is carried off in the form of vapour (*lead-fume*); and in order to condense this, the gases from the furnace are made to pass through flues, the aggregate length of which is sometimes three or four miles, before being allowed to escape up the chimney. When these flues are swept, many tons of lead are recovered in the forms of oxide and sulphide.

It has lately been asserted that the reactions stated above as being representative of the changes which occur in the Flintshire lead-smelting process, have no real existence. Instead, it is maintained, the greater part of the S is removed directly as SO_2, leaving a product containing about 3–5 per cent. of S, which is then liquated, when the greater part of the lead separates, much oxygen being at the same time absorbed, and a slag, having the composition PbS.PbO, formed. This must be thickened with lime and removed from the lead to prevent its sulphur from passing into the metal. It is also stated that a volatile compound, $PbS.SO_2$, is formed in the furnace, and is the cause of lead fume.

The treatment of galena in Bessemer converters, whereby the same reactions that occur in the Flintshire furnace could easily be effected, has been suggested.

(2) Poor lead ores, rich in silica, are roasted until nearly free from sulphur, mixed with coke and flux (iron ore and lime), and smelted in small blast-furnaces; the lead is thus reduced from its oxide by the coke, and the gangue is fluxed as ferrous and calcium silicates.

A small blast-furnace for this process is shown in Fig. 229. Air is supplied to the furnace through three blast-pipes (A), and the ore and fuel being charged in at B, the lead runs into a cavity (C) at the bottom of the furnace, whilst the slag flows

over into a reservoir (D) outside the furnace. The charge is sprinkled with water through the rose (E) fixed just above the opening into the chimney (F), to prevent it from being blown away by the current of air.

(3) In the third process for smelting lead ores, mostly adopted on the Continent, advantage is taken of the fact that iron will desulphurise galena at a high temperature; $PbS + Fe = Pb + FeS$. The galena is mixed with scrap iron (or, what comes to the same thing, iron ore and coke), and charged into a small blast-furnace.

262. Some varieties of lead, particularly those smelted from Spanish ores, are known as *hard lead*, their hardness being chiefly due to the presence of antimony; and since this hardness interferes materially with some of the uses of the metal, such lead is generally subjected to an *improving* or *calcining* process, in which the impurities are oxidised and removed, together with a portion of the lead, in the dross.*

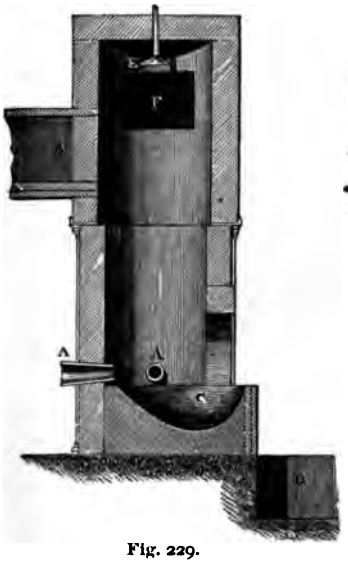


Fig. 229.

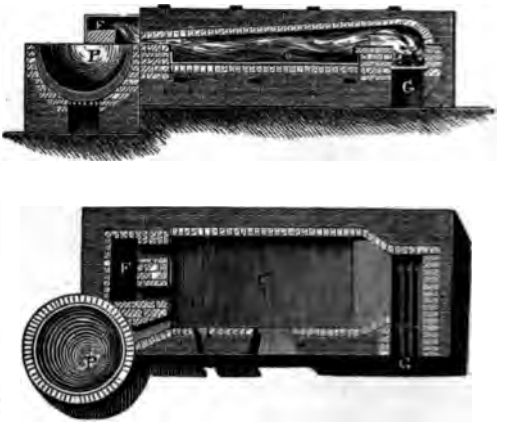


Fig. 230.

To effect this, 6 or 8 tons of the hard lead are fused in an iron pot (P, Fig. 230). and transferred to a shallow cast-iron pan (C) measuring about 10 feet by 5. In this pan, which is set in the hearth of a reverberatory furnace, and is about 8 inches deep nearest the grate, and 9 inches at the other end, the lead is kept in fusion by the flame which traverses it from the grate G to the flue F, for a period varying with the degree of impurity, some specimens being found sufficiently soft after a single day's calcination, whilst others must be kept in a state of fusion for three or four weeks. The workman judges of the progress of the operation by a peculiar flaky crystalline appearance assumed by a small sample on cooling. When sufficiently purified, the metal is run off and cast into pigs.

At first sight it is not intelligible how antimony should be removed from lead by calcination, since lead is the more easily oxidised metal.

* The following analyses illustrate the percentage composition of hard lead:

	Pb.		Sb.		Cu.		Fe.
English . . .	99.27	...	0.57	...	0.12	...	0.04
Spanish . . .	95.81	...	3.66	...	0.32	...	0.21

The result must be ascribed to the tendency of antimony to form an acid oxide, Sb_2O_5, which combines with the base oxide of lead. The dross (antimonate of lead) formed in this process, when reduced to the metallic state, yields an alloy of lead with 30 or 40 per cent. of antimony, which is much used for casting type furniture for printers.

263. *Extraction of silver from lead.*—The lead extracted from galena often contains a sufficient quantity of silver to allow of its being profitably extracted. Previously to the year 1829 this was practicable only when the lead contained more than 11 ounces of silver per ton, for the only process then known for effecting the separation of the two metals was that of cupellation, which necessitates the conversion of the whole of the lead into oxide, which has then to be separated from the

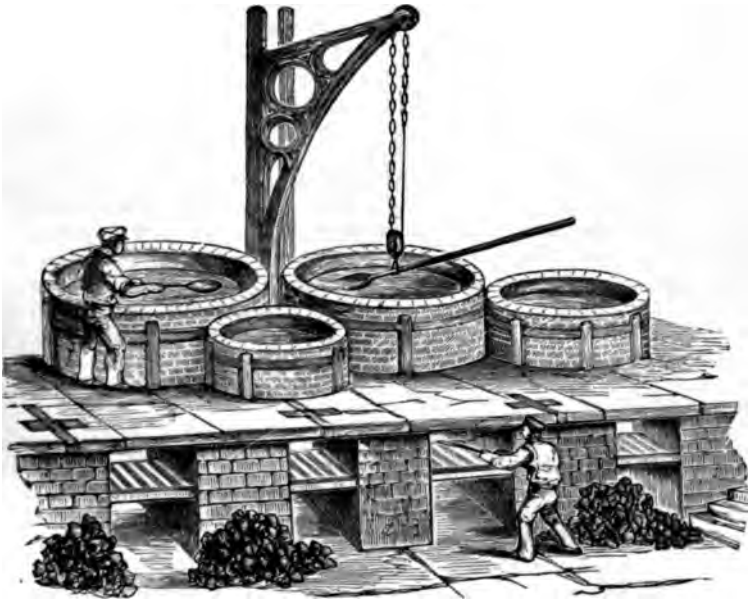


Fig. 231.—Pattinson's desilverising process.

silver, and again reduced to the metallic state, thus consuming so large an amount of labour that a considerable yield of silver must be obtained to pay for it. By the simple and ingenious operation known as *Pattinson's desilvering process*, a very large amount of the lead can be at once separated in the metallic state with little expenditure of labour, thus leaving the remainder sufficiently rich in the more precious metal to defray the cost of the far more expensive process of cupellation, so that 2 or 3 ounces of silver per ton can be extracted with profit. Pattinson founded his process upon the observation that when lead containing a small proportion of silver is melted and allowed to cool, being constantly stirred, a considerable quantity of the lead separates in the form of crystals containing a very minute proportion of silver, almost the whole of this metal being left behind in the portion still remaining liquid.

[illegible] [illegible] [illegible] [

h a gutter until the cupel is nearly filled with it; a film of oxide soon its appearance upon the surface of the lead, and is fused by the high tem-e. When the blast is directed upon the surface, it blows off this film of and supplies the oxygen for the formation of another film upon the clean c surface thus exposed. A part of the oxide of lead or litharge thus is at first absorbed by the porous material of the cupel, but the chief part forced by the blast through a channel cut for the purpose in the opposite that at which the blast enters, and is received, as it issues from A, in an essel placed beneath the surface. In proportion as the lead is in this r removed from the cupel, fresh portions are supplied from the adjoining g-pot, and the process is continued until about 5 tons of the alloy have lded.

upellation is not continued until the whole of the lead has been removed, il only 2 or 3 cwts. of that metal are left in combination with the whole of er (say 1000 ounces) contained 5 tons of alloy. The metal through a hole made in the of the cupel, which is then stopped up, so that a fresh may be introduced. The of oxide of lead which are volved during this process are off by a hood and chimney uated opposite to the blast of

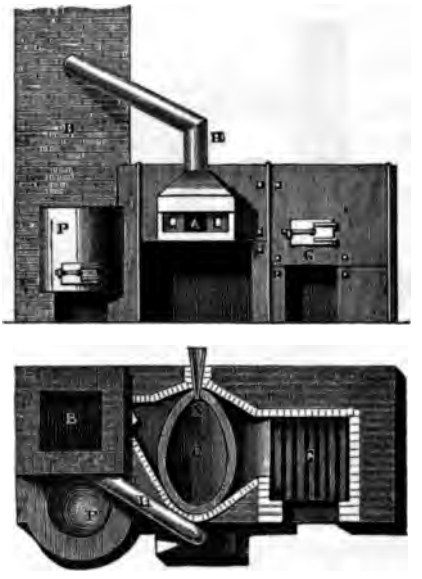


Fig. 232.—Cupellation furnace.

n three or four charges have upelled, so as to yield from 5000 ounces of silver alloyed or 8 cwts. of lead, the removal latter metal is completed in cupel, since some of the is carried off with the last s of litharge. The appear-ndicating the removal of the tion of lead are very striking; face of the molten metal, has been hitherto tarnished, s iridescent as the film of of lead thins off, and after-esplendently bright, and when e of refined silver is allowed it throws up from its surface ty of fantastic arborescent ences, caused by the escape of which has been mechanically d by the fused silver, and is given off during solidification.

itharge obtained from the cupelling furnaces is reduced to the metallic y mixing it with small coal, and heating it in a furnace similar to that em-in smelting galena.

On the small scale, lead may easily be extracted from galena by mixing 300 vith 450 grains of dried sodium carbonate and 20 grains of charcoal, intro-the mixture into a crucible, and placing in it two tenpenny nails, heads ards. The crucible is covered and heated in a moderate fire for about hour. The remainder of the nails is carefully removed from the liquid hich is then allowed to cool, the crucible broken, and the lead extracted ghed. In this process the sulphur of the galena is removed, partly by the of the carbonate and partly by the iron of the nails, the excess of sodium te serving to flux any silica with which the galena may be mixed.

o grains of galena may be mixed with 600 grains of sodium carbonate and ns of nitre (which oxidises the sulphur), and fused for half an hour.

certain if it contains silver, the button of lead is placed on a small bone-el (Fig. 233), and heated in a muffle (Fig. 235), until the whole of the lead ed and absorbed into the bone-ash of the cupel, leaving the minute globule

A gas muffle furnace, also capable of being used as a crucible furnace, is shown in Fig. 234.

Small globules of lead may be conveniently cupelled on charcoal before the blowpipe, by pressing some bone-ash into a cavity scooped in the charcoal, placing the lead upon its surface, and exposing it to a good oxidising flame (p. 156) as long as it decreases in size. If any copper be present, the bone-ash will show a green stain after cooling. Pure lead gives a yellow stain.

Fig. 233.—Cupel.

Fig. 234.—Muffle and crucible furnace.

Fig. 235.—Muffle furnace.

266. **Uses of lead.**—The employment of this metal for roofing, &c., has been already noticed. Its fusibility adapts it for casting type for printing, but it would be far too soft for this purpose; accordingly, *type-metal* consists of an alloy of 4 parts of lead with 1 of antimony. A similar alloy is used for the bullets contained in shrapnel shells, since bullets of soft lead would be liable to be jambed together, and would not scatter so well on the explosion of the shell. On the other hand, rifle bullets are made of very pure soft lead, in order that they may more easily take the grooves of the rifle.

Small shot are made of lead to which about 40 lbs. of arsenic per ton has been added. The arsenic dissolves in the lead, hardening it and causing it to form spherical drops when chilled. The fluid metal is poured through a sort of colander fixed at the top of a lofty tower (or at the mouth of a deserted coal shaft), and the minute drops into which the lead is thus divided are allowed to fall into a vessel of water, after having been chilled by the air in their descent. They are afterwards sorted, and polished in revolving barrels containing plumbago. If too little arsenic is employed, the shot are elongated or pyriform; and if the due proportion has been exceeded, their form is flattened or lenticular.

Composition tube ("compo-pipe") used by plumbers is made of lead hardened by a little antimony. *Solder* has been already noticed (p. 452).

Leaden vessels are much used in manufacturing chemistry, on account

of the resistance of this metal to the action of acids. Neither concentrated sulphuric,* hydrochloric, nitric, or hydrofluoric acid will attack lead at the ordinary temperature. The best solvent for the metal is nitric acid of sp. gr. 1.2, since the nitrate of lead, being insoluble in an acid of greater strength, would be deposited upon the metal, which it would protect from further action.

Lead is easily corroded in situations where it is brought in contact with air highly charged with carbonic acid gas, when it absorbs oxygen, forming oxide of lead, which combines with CO_2 and water to produce the basic carbonate of lead, $PbCO_3.Pb(OH)_2$. The lead of old coffins is often found converted into a white earthy-looking brittle mass of basic carbonate, with a very thin film of metallic lead inside it. The basic carbonate is formed as a crystalline silky-looking precipitate when a piece of clean lead is left in distilled water for a few minutes.

When lead is exposed to the joint action of air and of the acetic acid contained in beer, wine, cider, &c., it becomes converted into acetate of lead or sugar of lead, which is very poisonous. Hence the accidents arising from the reprehensible practice of sweetening cider by keeping it in contact with lead, and from the accidental presence, in beer and wine bottles, of shot which have been employed in cleansing them. The action of water upon leaden cisterns has been already noticed. Contact with air and sea-water soon converts lead into oxide and chloride.

267. **Oxides of lead.**—Five compounds of lead with oxygen are known—Pb_2O, PbO, Pb_2O_3, Pb_3O_4, PbO_2.

Lead suboxide, or *plumbous oxide*, Pb_2O, is obtained by heating lead oxalate; $2PbC_2O_4 = Pb_2O + CO + 3CO_2$. It is a black powder which is decomposed by acids, yielding plumbic salts and metallic lead.

The bright surface of lead soon tarnishes when exposed to the air, becoming coated with a dark film, which is believed to consist of suboxide of lead. In a very finely divided state, lead takes fire when thrown into the air, and is converted into oxide of lead.

The *lead pyrophorus*, for exhibiting the spontaneous combustion of lead, is prepared by placing some lead tartrate in a glass tube closed at one end (Fig. 236), drawing the tube out to a narrow neck near the open end, and holding it nearly horizontally, whilst the lead tartrate is heated with a gas or spirit flame as long as any fumes are evolved; the neck is then fused with a blowpipe flame and drawn off. Lead tartrate ($PbC_4H_4O_6$), when heated, leaves a mixture of metallic lead with charcoal, which prevents the lead from fusing into a compact mass. This mixture may be preserved unchanged in the tube for any length of time: but when the neck is broken off and the contents scattered into the air, they inflame at once, producing thick fumes of oxide of lead. Lead tartrate is prepared by adding solution of lead acetate to a solution of tartaric acid constantly stirred, as long as a precipitate is formed. The precipitated lead tartrate is collected upon a filter, washed several times, and dried at a gentle heat.

Fig. 236.

Lead monoxide, or *protoxide of lead*, PbO, is sometimes found in nature, crystallised in rhombic octahedra, and is prepared on a large scale by heating lead in air. When the metal is only moderately heated, the oxide forms a yellow powder (sp. gr. 9.2), which is known in

* It has been found that pure lead is slowly acted on by sulphuric acid, hydrogen being evolved. The presence of a little antimony almost entirely prevents the action.

commerce as *massicot*, but at a higher temperature the oxide melts, and on cooling forms a brownish scaly mass, which is called *litharge* (λίθος, *stone*; ἄργυρος, *silver*). The litharge of commerce often has a red colour, caused by the presence of some red oxide of lead; from 1 to 3 per cent. of finely divided metallic lead may also sometimes be found in it. When heated to dull redness, litharge assumes a dark brown colour, and becomes yellow on cooling. At a bright red heat it fuses, and readily attacks clay crucibles, forming a fusible silicate of lead, and soon perforating the sides. When boiled with distilled water, PbO is dissolved in small quantity, yielding a solution which is decidedly alkaline, and becomes turbid when exposed to the air, absorbing carbonic acid gas, and depositing lead carbonate. The presence of a small quantity of saline matter in the water hinders the dissolution of the oxide; but organic matter, and especially sugar, favours it. Oxide of lead is a powerful base, and has a strong tendency to form basic salts. Hot solutions of potash and soda dissolve it readily, and deposit it in pink crystals on cooling; according to some, such solutions contain sodium or potassium *plumbite*, K_2PbO_2.

Litharge, from its easy combination with silica at a high temperature, is much used in the manufacture of glass, and in glazing earthenware. The assayer also employs it as a flux. A mixture of litharge with lime is sometimes applied to the hair, which it dyes of a purplish-black colour, due to the formation of lead sulphide from the sulphur existing in hair. *Dhil mastic*, used by builders in repairing stone, is a mixture of 1 part of massicot with 10 parts of brick-dust, and enough linseed oil to form a paste; it sets into a very hard mass, which is probably due partly to the formation of lead silicate, and partly to the *drying* of the linseed oil by oxidation favoured by the oxide of lead.

Lead sesquioxide, Pb_2O_3, is obtained as a yellow precipitate by dissolving PbO in caustic soda and adding sodium hypochlorite. Cold HCl dissolves it to a yellow liquid, which slowly evolves chlorine. Nitric acid partly dissolves it, leaving a brown residue of PbO_2. Heat converts it into PbO.

Red lead, or *minium*, Pb_3O_4, is prepared by heating massicot in air to about 300° C, when it absorbs oxygen, and becomes converted into red lead. The massicot for this purpose is prepared by heating lead in a reverberatory furnace to a temperature insufficient to fuse the oxide which is formed, and rejecting the first portions which contain iron, cobalt and other metals more easily oxidisable than lead, as well as the last, which contain copper and silver, less easily oxidised than lead. The intermediate product is ground to a fine powder and suspended in water; the coarser particles are thus separated from the finer, which are dried, and heated on iron trays placed in a reverberatory furnace, till the requisite colour has been obtained. Minium is largely used in the manufacture of glass, whence it is necessary that it should be free from the oxides of iron, copper, cobalt, &c., which would colour the glass. It is also employed as a common red mineral colour, and in the manufacture of lucifer matches. Red lead becomes dark brown when heated, and regains its original colour when cooled.

When minium is treated with dilute nitric acid, lead nitrate, $Pb(NO_3)_2$, is obtained in solution, and peroxide of lead (PbO_2) is left as a brown powder, showing that minium is probably a compound of the oxide and

peroxide of lead. The minium obtained by heating massicot in air till no further increase of weight is obtained, has the composition $2PbO.PbO_2$ or Pb_3O_4, which would appear to represent pure minium; commercial minium, however, has more frequently a composition corresponding with $3PbO.PbO_2$, but when this is treated with potash, PbO is dissolved out, and $2PbO.PbO_2$ remains. Minium evolves oxygen at a red heat, becoming PbO; hence the necessity for keeping the temperature about 300° C. during its preparation. Hydrochloric acid, heated with minium, evolves chlorine by reaction with the PbO_2 contained in it, and leaves the white sparingly soluble $PbCl_2$ formed from the PbO contained in the Pb_3O_4. A mixture of dilute nitric acid and sugar, or some other oxidisable body, will dissolve minium entirely as $Pb(NO_3)_2$. Glacial acetic acid dissolves minium, without evolution of gas, to a colourless liquid, which deposits PbO_2 when exposed to air, or evaporated, or diluted; a hot saturated solution deposits colourless crystals of *lead tetracetate* $Pb(C_2H_3O_2)_4$ on cooling.

Peroxide, or *dioxide*, or *puce oxide of lead*, PbO_2, is found in the mineral kingdom as *heavy lead ore*, forming black, lustrous, six-sided prisms. It may be prepared from red lead by boiling it, in fine powder, with nitric acid, diluted with five measures of water, washing and drying. The dioxide of lead easily imparts oxygen to other substances; sulphur, mixed with six times its weight of PbO_2, may be ignited by friction; hence this oxide is a common ingredient in lucifer-match compositions. Its oxidising property is frequently turned to account in the laboratory; for example, in absorbing sulphur dioxide from gaseous mixtures by converting it into sulphate of lead; $PbO_2 + SO_2 = PbSO_4$. Dioxide of lead is not dissolved by dilute acids, and has no basic properties, although certain salts of the type PbX_4 are known; it is even sometimes called plumbic anhydride, for it acts upon potassium hydroxide, yielding potassium plumbate ($K_2PbO_3.3H_2O$.), which has been crystallised from an alkaline solution, but is decomposed by pure water.* Lead dioxide evolves Cl from HCl when heated, and gives, at first, a brown solution (containing $PbCl_4$) which yields a brown precipitate with ammonia, but if the solution be boiled till all the Cl is expelled, it becomes colourless $PbCl_2$, and gives a white precipitate with ammonia. PbO is converted into PbO_2 by ozone and by hydrogen peroxide.

Lead peroxide is almost the only available material for making the "active mass" for *electric accumulators* or *storage* or *secondary cells*. When two lead plates, one coated with PbO_2, are immersed in dilute H_2SO_4 an electrical pressure of about 2 volts is created, and if the current be used, both plates become coated with $PbSO_4$ before the energy ceases to flow. The ultimate change may be expressed thus: $-Pb + PbO_2 + 2H_2SO_4 = 2PbSO_4 + 2H_2O$. If, when this stage has been reached, current be passed into the cell in the direction opposite to that of the current which has been used, the $PbSO_4$ on the one plate will be oxidised to H_2SO_4 and PbO_2, while that on the other will be reduced to Pb and H_2SO_4. Hence the cell will again be ready to deliver current, which, however, will be smaller in amount than that used to charge the cell by the inevitable loss due to resistance, etc. It will be seen that during discharge the free H_2SO_4 disappears from the cell, while during charging it is liberated again; thus by watching the indications of a

* Advantage is taken of the tendency for PbO to absorb O when heated with an alkali in *Kassner's oxygen process*. A mixture of CaO and PbO is heated in air, $CaPbO_3$ being produced. This is heated (below 100° C.) in CO_2, when it becomes $CaCO_3$ and PbO_2; the latter is then made to part with half its oxygen by a red heat, after which the $CaCO_3$ is causticised by being heated in a current of steam. The mixture of CaO and PbO thus regenerated is put through the same cycle of operations.

hydrometer immersed in the liquid, the progress of either operation may be judged.

Lead hydroxide, $Pb(OH)_2$, has not been obtained, but $Pb(OH)_2.PbO$ is formed as a white precipitate when air and water, free from CO_2, attack lead, hydrogen peroxide being formed at the same time nearly in the proportion represented by the equation—$Pb + 2H_2O + O_2 = Pb(OH)_2 + H_2O_2$ (*cf.* footnote, p. 63). The same hydroxide is precipitated by alkalies from solutions of lead salts. It becomes PbO when heated to 145° C. The compound $Pb(OH)_2.2PbO$ crystallises in octahedra from a solution of basic lead acetate mixed with ammonia.

Lead nitrate, $Pb(NO_3)_2$, crystallises in white octahedra from a solution of lead or its oxide in dilute nitric acid. It dissolves easily in water, but not in nitric acid or in alcohol. It is employed in dyeing and calico-printing. Several sparingly soluble *basic lead nitrates* are known. When digested with water and metallic lead, the nitrate gives a yellow solution, which deposits yellow scaly crystals of the compound $Pb.OH.NO_3.Pb.OH.NO_2$.

268. **Lead carbonate**, $PbCO_3$, is found in nature, as *cerussite*, in transparent rhombic crystals isomorphous with aragonite. It may be precipitated by mixing solutions of ammonium carbonate and lead acetate, or by passing CO_2, into a weak solution of lead acetate. Potassium and sodium carbonates precipitate basic lead carbonates.

White lead, or *ceruse*, is a basic carbonate, or combination of lead carbonate, $PbCO_3$, with variable proportions of lead hydroxide, $Pb(OH)_2$. This substance is a constant product of the corrosive action of air and water upon the metal. Its formation is, of course, very much encouraged by the presence of organic matters in a state of decay, which evolve CO_2.

White lead is manufactured on the large scale by several processes, which depend, however, upon the same principle, namely, the formation of a basic lead salt, which is subsequently decomposed by CO_2. The chemistry of the commonest process may be stated as follows; lead oxide, PbO, with acetic acid, $HC_2H_3O_2$, yields lead acetate $Pb(C_2H_3O_2)_2$, conveniently written $Pb\bar{A}_2$. This combines with lead hydroxide, forming basic lead acetate, $Pb\bar{A}_2.2Pb(OH)_2$. This is decomposed by carbonic acid gas, yielding basic lead carbonate and normal lead acetate; $3[Pb\bar{A}_2.2Pb(OH)_2] + CO_2 = 2[2PbCO_3.Pb(OH)_2] + 3Pb\bar{A}_2 + 4H_2O$. The normal acetate, in contact with lead, atmospheric oxygen, and water is converted into the basic acetate; $Pb\bar{A}_2 + Pb_2 + O_2 + 2H_2O = Pb\bar{A}_2.2Pb(OH)_2$; this is again acted on by CO_2, and the process is continuous. To effect these changes, lead is exposed to the simultaneous action of air, water vapour, carbon dioxide, and acetic acid vapour.

In the oldest process (still used to make the best pigment), commonly known as the Dutch process, metallic lead, in the form of square gratings cast from the purest lead, is placed over earthen pots containing a small quantity of common vinegar; a number of these pots being built up into heaps, together with alternate layers of dung or spent tan, the heaps are entirely covered up with the same material. The metal is thus exposed to conditions most favourable to its oxidation, viz., a very warm and moist atmosphere produced by the fermentation of the organic matters composing the heap, and the presence of a large quantity of acid vapour generated from the acetic acid of the vinegar. The lead is therefore soon converted into oxide, a portion of which unites with the acetic acid to form the tribasic acetate of lead, which is then decomposed by the carbonic acid gas, evolved from the fermenting dung or tan, yielding carbonate of lead, which combines with another portion of the oxide of lead and water to form the white lead. The neutral acetate of lead left after the removal of the oxide of lead from the tribasic acetate, is now ready to take up an additional quantity of the oxide,

and the process is thus continued until, in the course of a few weeks, the lead has become coated with a very thick crust of white lead; the heaps are then destroyed, the crust detached, washed to remove adhering acetate of lead, ground to a paste with water, and dried. Rolled lead is not so easily converted as cast lead.

Other processes for making white lead exist, but for a description of them larger works on technical Chemistry must be consulted.

The usual composition of white lead is expressed by the formula $Pb(OH)_2.2PbCO_3$, though other basic carbonates of lead are often mixed with it.

White lead being very poisonous, its use by painters and others is generally attended with symptoms of lead poisoning, arising in many cases, probably, from neglecting to wash the hands before eating, the effect of lead being *cumulative*, so that minute doses may show their combined action after many days. Diluted sulphuric acid and solutions of the sulphates of magnesia and the alkalies are sometimes taken internally to counteract its effect; they are of doubtful efficacy.

All paints containing lead, and cards glazed with white lead, are blackened even by minute quantities of sulphuretted hydrogen, from the production of black sulphide of lead. If the blackened surface remain exposed to the light and air, it is bleached again, the sulphide of lead (PbS) being oxidised and converted into white sulphate of lead ($PbSO_4$), but this does not happen in the dark. A little sulphide of lead or powdered charcoal is sometimes mixed with commercial white lead to give it a bluish tint. It is probable that white lead owes a part of its value in oil-painting to the formation of a lead-salt with the fatty acid. Its "covering" power is due to its amorphous character, which renders it completely opaque. Pure white lead is easily soluble in acetic and dilute nitric acids.

Lead sulphate, $PbSO_4$, is found naturally as *anglesite* or lead vitriol, in transparent rhombic prisms (sp. gr. 6.3) isomorphous with celestine and heavy spar, and is obtained as a heavy granular precipitate when sulphuric acid is added to a salt of lead. Stirring much promotes the precipitation. Lead sulphate is very slightly soluble in water, and even less so in dilute sulphuric acid and in alcohol. It is soluble in strong sulphuric and hydrochloric acids, in sodium chloride and thiosulphate, and in ammonium acetate and tartrate. At a red heat it fuses without decomposition.

An *acid lead sulphate*, $PbH_2(SO_4)_2.Aq$, has been crystallised. The minerals *lanarkite* and *leadhillite* are compounds of sulphate and carbonate of lead, $PbSO_4(PbCO_3)_2.H_2O$. The chromates of lead have been already noticed.

Lead phosphate, $Pb_3(PO_4)_2$, and *arsenate*, associated with lead chloride and carbonate, are found in certain minerals.

269. *Lead chloride* ($PbCl_2$=2 vols.) forms the mineral termed *horn lead*. It is one of the few chlorides which are not readily soluble in water, and is precipitated when hydrochloric acid or a soluble chloride is added to a solution of lead. Boiling water dissolves about $\frac{1}{30}$th of its weight of lead chloride, and deposits it in beautiful shining white needles on cooling. Cold water dissolves abont $\frac{1}{135}$th of its weight. It fuses easily (510° C.) and solidifies again to a horny mass, like fused silver chloride. It is converted into vapour at a high temperature. Lead chloride dissolves easily in strong HCl, and is precipitated by water. The solution of lead chloride in water is precipitated by adding strong HCl; hence, a dilute HCl solution, when cold, retains very little lead chloride. Like silver chloride, lead chloride is soluble in sodium thiosulphate.

The *lead oxychloride* ($PbCl_2.PbO$) is formed when lead chloride is heated in air, and occurs in nature as *matlockite*. *Pattinson's oxychloride*, PbCl.OH, is sometimes

employed as a substitute for white lead in painting, being prepared for this purpose by decomposing finely powdered galena with concentrated hydrochloric acid ($PbS + 2HCl = PbCl_2 + H_2S$), washing the resulting lead chloride with cold water, dissolving it in hot water, and adding lime-water, which precipitates the oxychloride; $2PbCl_2 + Ca(OH)_2 = 2PbCl(OH) + CaCl_2$.

Cassel yellow (Paris yellow, patent yellow, mineral yellow) is another oxychloride of lead ($PbCl_2.7PbO$), prepared by heating a mixture of litharge and sal-ammoniac. It has a fine golden-yellow colour, is easily fused, and crystallises in octahedra on cooling. *Turner's yellow*, $PbCl_2.3PbO$, is made by allowing a strong solution of NaCl to react with PbO. The mineral *mendipite* is an oxychloride of lead ($PbCl_2.2PbO$) which occurs in colourless prismatic crystals.

Lead tetrachloride, $PbCl_4$, probably exists in the brown solution of PbO_2 in cold HCl, which gives a brown precipitate of PbO_2 when diluted. A solution made by suspending $PbCl_2$ in water and passing chlorine may be supposed to contain chloroplumbic acid, H_2PbCl_6, for with salts of rubidium and ammonium it yields yellow crystalline precipitates of Rb_2PbCl_6 and $(NH_4)_2PbCl_6$ respectively. When the latter is added to strong H_2SO_4 a heavy oil (sp. gr. 3.18) separates; this is $PbCl_4$.

Lead chlorobromide (PbBrCl) has been found in crystals resembling lead chloride among the furnace-products in smelting lead carbonate ore.

Lead iodide (PbI_2) is obtained as a bright yellow precipitate on mixing solutions of nitrate or acetate of lead and potassium iodide. If it be allowed to settle, the liquid poured off, and the precipitate dissolved in boiling water (with one or two drops of hydrochloric acid), it forms a colourless solution, depositing golden scales as it cools. Hydriodic acid converts metallic lead into PbI_2. Like mercuric iodide, PbI_2 dissolves in the alkali iodides. When heated, it becomes red, then black, fuses, and becomes a yellow crystalline mass on cooling. It is decomposed by light with liberation of iodine.

270. **Sulphides of lead.**—*Lead sulphide*, PbS, is found as galena (p. 459). It fuses when strongly heated, and vaporises in a current of gas, condensing in small crystals. When heated in air, it is converted into a mixture of PbO and $PbSO_4$. Strong HCl dissolves it when heated, evolving H_2S. Nitric acid dissolves it partly as lead nitrate, leaving some undissolved lead sulphate mixed with sulphur. Lead sulphide is obtained as a black precipitate when hydrosulphuric acid or a soluble sulphide acts upon a solution containing lead, even in minute proportion.

A *persulphide of lead*, the composition of which has not been ascertained, is formed as a red precipitate when a solution of lead is mixed with a solution of an alkaline sulphide saturated with sulphur (or with solution of ammonium sulphide which has been kept till it has acquired a red colour). It is probably PbS_5.

Lead chlorosulphide ($PbS.PbCl_2$) is obtained as a bright red precipitate when hydrosulphuric acid is added in small quantity to a solution of lead chloride in hydrochloric acid, or when freshly precipitated PbS is heated with solution of $PbCl_2$. It is decomposed by hot water.

Lead selenide (PbSe) occurs associated with the sulphide in some lead ores; it much resembles galena, and has the same crystalline form.

Tin group of metals.—This group comprises Ti, Zr, Ce, Th, Ge, Sn and Pb. These metals belong to the group of elements which includes C and Si, the higher salt-forming oxide being RO_2, which in most cases behaves as a feeble acid oxide, resembling CO_2 and SiO_2. Their tetrafluorides have a tendency to combine with the alkali fluorides to form compounds which recall the salts of hydrofluosilicic acid, and their tetrachlorides form similar double salts with alkali chlorides (*e.g.*, $2NH_4Cl.PbCl_4$, $2KCl.SnCl_4$), which resemble the double chlorides formed by metals of the platinum group.

Thallium, Tl = 202.6.

271. The discovery of this metal in 1861 was one of the first results of the application of the new method of testing by observation of coloured lines in the

spectrum of a flame, described at p. 328. Crookes was examining the spectrum obtained by holding in the flame of a Bunsen burner the deposit formed in the flues of a sulphuric acid chamber, in which pyrites was employed as the source of sulphur. A green line appeared in the spectrum, which a less acute and practised observer might have mistaken for one of the lines due to barium (see Fig. 213), with which it nearly coincides in position; but the line was much brighter than that of barium, and on instituting a searching analysis of the deposit, a metal was obtained which did not agree in properties with any hitherto described, and was named *thallium* from θαλλός, *a young shoot*, in allusion to the vernal green colour of its spectrum line. It has since been detected in several mineral waters; but the pyrites obtained from Spain and Belgium appears to be its best source. From the flue-dust of the sulphuric acid chambers the metal is extracted by a simple process, but large quantities must be operated on to obtain any considerable amount. The deposit is treated with boiling water, and the solution mixed with much strong hydrochloric acid, which precipitates the thallium as thallous chloride (TlCl); this is converted into acid thallous sulphate ($TlHSO_4$) by treatment with sulphuric acid, and this salt having been purified by recrystallisation, is decomposed by zinc, which precipitates metallic thallium in a spongy form, fusible into a compact mass in an atmosphere of coal gas.

Thallium is now classed with the metals of the aluminium group (p. 393), although it differs considerably from these in the stability of its lower oxide Tl_2O.

In external characters thallium is very similar to lead; (sp. gr. 11.8.; m. p. 290° C.; volatile below 800° C.); but it tarnishes much more rapidly when exposed to air, and the streak which it makes on paper soon becomes yellowish, being converted into thallous oxide, Tl_2O. If a tarnished piece of the metal be allowed to touch the tongue, a strongly alkaline taste is perceived, for the *thallous oxide* (Tl_2O) is very soluble in water, so that the tarnished metal becomes bright when immersed in water. If granulated thallium be exposed to moist air in a warm place, it absorbs oxygen and CO_2. On boiling with water and filtering, the alkaline solution deposits white needles of *thallous carbonate* (Tl_2CO_3), and afterwards yellow needles of *thallous hydroxide* (TlOH). The ready solubility of the oxide seemed to require thallium to be classed among the alkali-metals, a view which was encouraged by the circumstance that its specific heat proved it to be monatomic, like potassium and sodium. But thallium appears to be more nearly related to another monatomic metal, silver, by the sparing solubility of its chloride and the insolubility of its sulphide. The circumstance that it may be kept unaltered in water, and may be precipitated from its salts by zinc, at once removes it from the group of alkali-metals. The ready solubility of its oxide in water is only an exaggeration of the behaviour of the oxides of lead and silver, both of which dissolve slightly in water, yielding alkaline solutions. Moreover, its hydroxide is far less stable than those of potassium and sodium, for it becomes Tl_2O when dried *in vacuo* over oil of vitriol. Dilute H_2SO_4 acts on thallium as on zinc, evolving hydrogen. It is not much affected by dilute HNO_3 in the cold; even on heating, the action is slow unless the acid is very weak. On cooling, the solution becomes filled with needles of *thallous nitrate*. Thallium burns in oxygen with a beautiful green flame, and the thallous chlorate has been recommended for the manufacture of green fires in place of barium chlorate (page 186).

Thallous sulphate, Tl_2SO_4, is obtained by dissolving thallium in sulphuric acid and evaporating; the acid sulphate, $TlHSO_4$, first produced, being decomposed by further heating. Tl_2SO_4 is isomorphous with K_2SO_4, and it forms *thallous alum*, $TlAl(SO_4)_2.12Aq$, crystallising like potash-alum. *Thallous chloride*, TlCl, resembles lead chloride, being precipitated by adding HCl to a solution of a thallous salt, and being dissolved by boiling water, from which it crystallises on cooling. *Thallous iodide*, TlI, is obtained as a yellow precipitate on adding potassium iodide to a thallous salt; when dried and heated, it fuses to a red liquid, which remains red after solidifying, and changes, after a time, to yellow. When spread on paper, the yellow iodide becomes red when heated, and remains red on cooling, but becomes yellow when rubbed with a hard body. *Thallous sulphide*, Tl_2S, is deposited as a brownish-black precipitate on adding ammonium sulphide to a thallous salt. *Thallic oxide*, Tl_2O_3, is obtained by adding sodium hypochlorite to thallous chloride mixed with excess of sodium carbonate. It is a dark red substance, which evolves oxygen and leaves thallous oxide when heated. It is also a basic oxide, its sulphate having the composition $Tl_2(SO_4)_3.H_2O.6Aq$. *Thallic chloride*, $TlCl_3$, is formed by heating thallium in excess of chlorine; it is soluble

and crystallisable. By passing Cl through a solution of KOH in which Tl_2O_3 is suspended, a liquid is obtained which gives a violet precipitate with barium salts; this precipitate is alleged to contain TlO_2.

Thallous silicate can take the place of alkali silicate in glass, and *thallium glass*, made from thallous carbonate, red lead and sand is similar to flint-glass, but has a higher sp. gr. (5.6) and refractive index. It is also more fusible and harder than ordinary flint-glass.

Salts of thallium, like those of lead, are poisonus.

COPPER.

$Cu'' = 63.1$ parts by weight.

272. Metallic copper is met with in nature more abundantly than *metallic* iron, though the compounds of the latter metal are of more frequent occurrence than those of the former.* A very important vein of metallic copper, of excellent quality, occurs near Lake Superior, in North America, from which 6000 tons were extracted in 1858. Metallic copper is also sometimes found in Cornwall, and *copper sand*, containing metallic copper and quartz, is imported from Chili.

The most important English ore of copper is *copper pyrites*, which is a double sulphide, containing copper, iron, and sulphur in the proportions indicated by the formula $Cu_2S.Fe_2S_3$. It may be known by its beautiful brass-yellow colour and metallic lustre. Copper pyrites is found in Cornwall and Devonshire, and is generally associated with arsenical pyrites ($FeS_2.FeAs_2$), tin-stone (SnO_2), quartz, fluor spar, and clay. A very attractive variety of copper pyrites is called *variegated copper ore*, or *peacock copper*, in allusion to its rainbow colours; its simplest formula is Cu_3FeS_3. This variety is found in Cornwall and Killarney.

Copper glance (Cu_2S) is another Cornish ore of copper, of a dark grey colour and feeble metallic lustre.

Grey copper ore, also abundant in Cornwall, is essentially a compound of the sulphides of copper and iron with those of antimony and arsenic, but it often contains silver, lead, zinc, and sometimes mercury.

Malachite, a basic carbonate of copper, is imported from Australia (Burra-Burra), and is also found abundantly in Siberia. Green malachite, the most beautifully veined ornamental variety, has the composition $CuCO_3.Cu(OH)_2$, and blue malachite is $2CuCO_3.Cu(OH)_2$.

Red copper ore (Cu_2O) is found in West Cornwall, and the black oxide (CuO) is abundant in the north of Chili.

273. The seat of English copper smelting is at Swansea, which is situated in convenient proximity to the bituminous coal employed in the furnaces. The chemical process by which copper is extracted from the ore includes three distinct operations—(1) the *roasting*, to expel the arsenic and part of the sulphur, and to convert the sulphide of iron into oxide of iron, the copper remaining as sulphide; (2) the *fusing with silica*, to remove the oxide of iron as silicate, and to obtain the copper in combination with sulphur only; and (3) the *roasting* of this combination

* Copper is not at all frequently found in animals or vegetables; but Church has made the remarkable observation that the red colouring-matter (*turacine*) of the feathers of the plantain-eater (*touraco*) contains as much as 7 per cent. of copper. It has also been found in the blood of the cuttle-fish, as *hæmocyanin*, which is blue in its oxidised condition in the arterial blood, and colourless in the venous blood.

of copper with sulphur, in order to expel the latter and obtain metallic copper by the process of self-reduction, $Cu_2S + 2CuO = Cu_4 + SO_2$.

The details of the smelting process appear somewhat complicated, because it is divided into several stages to allow of the introduction of the different varieties of ore to be treated. Thus, the first roasting process is unnecessary for the oxides and carbonates of copper, and the fusion with silica is not needed for those ores which are free from iron, so that they may be introduced at a later stage in the operations. Owing to the fact that rich ores of copper and copper precipitates are now much worked, the omission of the earlier processes is frequently practised, the ore being directly smelted to *white metal* (*fine metal*) as described below.

The processes of the older practice could be reduced in number if the original ore were a pure copper pyrites, but since the ores as worked always contain a larger proportion of iron and sulphur than copper pyrites does, the first two operations are designed to produce a material (coarse metal) which shall be, in effect, a pure copper pyrites.

(1) *Calcining* or *roasting the ore to expel arsenic and part of the sulphur.*—The ores having been sorted, and broken into small pieces, are mixed so as to contain from 8 to 10 per cent. of copper, and roasted, in quantities of about three tons, for at least twelve hours, on the spacious hearth (H, Fig. 237) of a reverberatory furnace

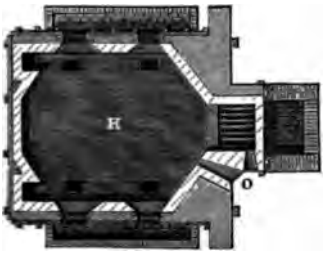


Fig. 237.

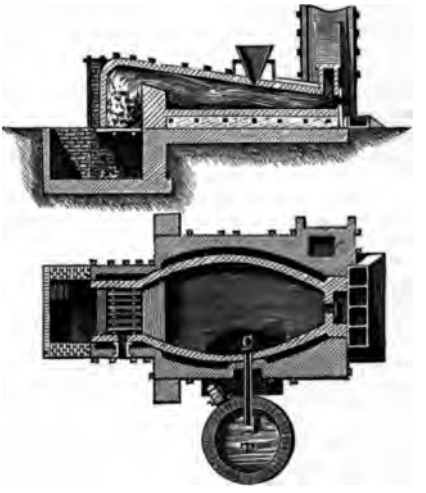


Fig. 238.

(Fig. 109, p. 132) at a temperature insufficient for fusion, being occasionally stirred to expose them freely to the action of the air, which is admitted into the furnace through an opening (O) in the side of the hearth upon which the ore is spread. The oxygen of the air converts a part of the sulphur into SO_2, and the bulk of the As into As_4O_6, which passes off in the form of vapour. A part of the sulphide of iron is converted into ferrous sulphate ($FeSO_4$) by absorbing oxygen at an early stage of the process, and this sulphate is afterwards decomposed at a higher temperature, evolving SO_2 and SO_3, and leaving oxide of iron. A portion of the sulphide of copper is also converted into oxide of copper during the roasting, so that the roasted ore consists essentially of a mixture of oxide and sulphide of copper with oxide and sulphide of iron. Since the sulphide of iron is more easily oxidised than sulphide of copper, the greater part of the latter remains unaltered in the roasted ore.

During the roasting of copper ore dense white fumes escape from the furnaces. This *copper smoke*, as it is termed, contains As_4O_6, SO_2, SO_3, and HF, the latter being derived from the fluor spar associated with the ore: if allowed to escape, these fumes seriously contaminate the air in the neighbourhood, so that they are usually condensed in flues and *rain-chambers* by showers of water.

(2) *Fusion for coarse metal to remove the oxide of iron by dissolving it with silica at a high temperature.*—The roasted ore is now mixed with *metal slag* from process 4, and with ores containing silica and oxides of copper, but no sulphur ; the mixture is introduced into the *ore furnace* (Fig. 238) (the hearth of which is made narrower than that of the roasting furnace, since a higher temperature is required) and fused for five hours at a higher temperature than that employed in the previous operation. In this process fluor spar is sometimes added in order to increase the fluidity of the slag.

The oxide of copper attacks the sulphide of iron still contained in the roasted ore, with formation of sulphide of copper and oxide of iron, but since there is more sulphide of iron present than the oxide of copper can decompose, the excess of sulphide of iron combines with the sulphide of copper to form a fusible compound, which separates from the slag, and collects in the form of a *matte* or *regulus* of *coarse metal*, in a cavity (C) on the hearth of the furnace : it is run out into a tank of water (T) in order to granulate it, so that it may be better fitted to undergo the next operation.

The oxide of iron combines with the silica contained in the charge, to form a fusible ferrous silicate (*ore-furnace slag*), which is raked out into moulds of sand, and cast into blocks used for rough building purposes in the neighbourhood.

The composition of the coarse metal corresponds pretty closely with the formula $CuFeS_2$. It contains from 33 to 35 per cent. of copper ; whilst the original ore, before roasting, is usually sorted so that it may contain about 8.5 per cent.

The ore-furnace *slag* is approximately represented by the formula $FeO.SiO_2$: but it contains a minute proportion of copper, as is shown by the green efflorescence on the walls in which it is used around Swansea. Fragments of quartz are seen disseminated through this slag.

(3) *Calcination of the coarse metal to convert the greater part of the sulphide of iron into oxide.*—The granulated coarse metal is roasted at a moderate temperature for twenty-four hours, as in the first operation, so that the oxygen of the air may decompose the sulphide of iron, removing the sulphur as sulphuric acid, and leaving the iron in the form of oxide.

(4) *Fusion for white metal to remove the whole of the iron as silicate.*—The roasted coarse metal is mixed with *roaster* and *refinery* slags from processes 5 and 6, and with ores containing carbonates and oxides of copper, and fused for six hours, as in the second operation. Any sulphide of iron which was left unchanged in the roasting is now converted into oxide of iron by the oxide of copper, the latter metal taking the sulphur. The whole of the oxide of iron combines with the silica to form a fusible slag, the composition of which is approximately represented by the formula $3FeO.2SiO_2$.

The *matte* or *regulus* of *white metal*, which collects beneath the slag, is nearly pure cuprous sulphide (Cu_2S). The white metal is run into sand-moulds and cast into ingots. The tin and other foreign metals usually collect in the lower part of the ingot, so that, for making *best selected copper*, the upper part is broken off and worked separately, the inferior copper obtained from the lower part of the ingot being termed *tile-copper*. The ingots of white metal often contain beautiful tufts of metallic copper in the form of *copper moss*.

The slag separated from the white metal (*metal slag*) is much more fluid than the ore-furnace slag, and contains so much silicate of copper that it is preserved for use in the melting for coarse metal.

(5) *Roasting the white metal to remove the sulphur and obtain blister copper.*—The ingots of white metal (to the amount of about 3 tons) are placed upon the hearth of a reverberatory furnace, and heated for four hours to a temperature just below fusion, so that they may be oxidised at the surface, the sulphur passing off as sulphurous acid gas, and the copper being converted into oxide. During this roasting the greater part of the arsenic, generally present in the fine metal, is expelled as As_4O_6. The temperature is then raised, so that the charge may be completely fused, after which it is lowered again till the twelfth hour. The oxide of copper now acts upon the sulphide of copper to form metallic copper and sulphurous acid gas, which escapes, with violent ebullition, from the melted mass ; $Cu_2S + 2CuO = SO_2 + Cu_4$. When this ebullition ceases, the temperature is again raised so as to cause the complete separation of the copper from the slag, and the metal is run out into moulds of sand. Its name of *blister copper* is derived from

the appearance caused by the escape of the last portions of SO_2 from the metal when solidifying in the mould.

The slag (*roaster slag*) is formed in this operation by the combination of a part of the oxide of copper with silica derived from the sand adhering to the ingots and from the hearth of the furnace. The slag also contains the silicates of iron and of other metals, such as tin and lead, which might have been contained in the white metal. This slag is used again in the melting for white metal.

(6) *Refining to remove foreign metals.*—This process consists in slowly fusing 7 or 8 tons of the blister copper in a reverberatory furnace, so that the air passing through the furnace may remove any remaining sulphur as sulphurous acid gas, and may oxidise the small quantities of iron, tin, lead, &c., present in the metal. Of course, a large proportion of the copper is oxidised at the same time, and the cuprous oxide, together with the oxides of the foreign metals, combine with the silica (from the hearth or from adhering sand), to form a slag which collects upon the surface of the melted copper.* A portion of the cuprous oxide is dissolved by the metallic copper, rendering it brittle or *dry copper*.

(7) *Toughening or poling to remove a part of the oxygen and bring the copper to tough-pitch.*—After about twenty hours the slag is skimmed from the metal, a quantity of anthracite is thrown over the surface to prevent further oxidation, and the metal is *poled—i.e.*, stirred with a pole of young wood—until a small sample, removed for examination, presents a peculiar silky fracture, indicating it to be at *tough-pitch*, when it is cast into ingots.

Products obtained in smelting Ores of Copper.

In 100 parts.	Ore.	Roasted Ore.	Coarse Metal.	Roasted Coarse Metal.	White Metal.	Blister Copper.	Refined Copper.	Tough-pitch Copper.
		(1)	(2)	(3)	(4)	(5)	(6)	(7)
Copper .	8.2	8.6	33.7	33.7	77.4	98.0	99.4	99.6
Iron . .	17.9	17.6	33.6	33.6	0.7	0.5	trace	trace
Sulphur .	19.9	12.5	29.2	13.0	21.0	0.2	trace	trace
Oxygen .	1.0	4.5	...	11.0	...	...	0.4	0.03
Silica . .	34.3	34.3						

Slags.	Ore Furnace.		Metal.	Roaster.	Refinery.	
	(2)		(4)	(5)	(6)	
Oxide of iron (FeO) . .	54.0		56.0	28.0	3.1	
Suboxide of copper (Cu_2O) .	0.5		0.9	16.9	39.2	
Silica	45.0		33.8	47.5	47.4	

The chemical change during the poling appears to consist in the removal of the oxygen contained in the cuprous oxide present in the metal, by the reducing action of the combustible gases disengaged from the wood. The presence of a small proportion of cuprous oxide is said to confer greater toughness upon the metal, so that if the poling be continued until the whole of the oxygen is removed, *over-poled copper* of lower tenacity is obtained. On the other hand, the brittleness of *under-poled copper* is due to the presence of cuprous oxide in too large proportion. *Tough-cake copper* is that which has been poled to the proper extent.

The addition of about 0.07 per cent. of phosphorus, as copper phosphide, before

* When the removal of arsenic, which forms an acid oxide, is specially desired, it is advantageous to line the hearth with a basic material, such as that used in the basic steel processes.

the final poling, shortens the process and increases the density of the metal. The copper phosphide is made by dissolving about 7 per cent of phosphorus in melted copper.

When the copper is intended for rolling, a small quantity (not exceeding ½ per cent.) of lead is generally added to it before it is ladled into the ingot moulds. Apparently the oxide of lead formed by the action of the air assists in removing some of the impurities in the form of slag (*scorification*).

The chemical changes which take place during the above processes will be more clearly understood after inspecting the table on page 477, which exhibits the composition of the products obtained at different stages of the process, these being distinguished by the same numerals as were employed in the above description.

Blue metal is the term applied to the regulus of white metal (from process 4) when it still contains a considerable proportion of sulphide of iron, in consequence of a deficient supply of oxide of copper in the furnace. *Pimple metal* is obtained in the same operation when the oxide of copper is in excess, so that a portion of the copper is reduced, as in process 5, with evolution of sulphurous acid gas, which produces the pimply appearance in escaping. The reduced copper gives a reddish colour to the pimple copper. *Coarse*, or *black copper*, is a similar intermediate stage between white metal and blistered copper. *Tile copper* is that extracted from the bottoms of the ingots of white metal, when the tops have been detached for making best selected copper. *Rosette* or *rose copper* is obtained by running water upon the toughened metal, so as to enable the metal to be removed in films. *Anglesea* or *Mona copper* is a very tough copper, reduced by metallic iron from the *blue water* of the copper mines, which contains sulphate of copper.

The application of the Bessemer converter to the refining of blister copper has been attempted, but the impurities to be oxidised are incapable of giving, by their combustion, a temperature sufficiently high to keep the copper in fusion. The converter is, however, employed on the Continent for the conversion of fused white metal into blister copper, there being sufficient sulphur in the white metal to yield a temperature high enough to maintain the fusion of the copper.

For the extraction of copper from poor ores (3 per cent. Cu) a *wet method* is generally adopted. This is rendered economically possible by the fact that when moist copper sulphide is exposed to the air* it becomes oxidised to copper sulphate, which may be dissolved in water. The recovery of the copper from the solution is effected by the introduction of pig-iron, when this metal takes the place of the copper which is precipitated, $CuSO_4 + Fe = FeSO_4 + Cu$. The *copper precipitate* thus obtained is melted and refined. Electrolytic deposition of the copper from the solution is also practised.

Two other methods of dissolving the copper sulphide from the ore are employed. In the one, the ore is treated with a solution of a ferric salt containing common salt. The former converts the Cu_2S of the ore into Cu_2Cl_2, which is dissolved by the solution of salt; $Cu_2S + Fe_2Cl_6 = 2FeCl_2 + Cu_2Cl_2 + S$. The dissolved copper is then precipitated by iron. In the second method (applied to the *spent pyrites* of the vitriol works, p. 226) the ore is submitted to a *chlorinating roasting*—that is to say, it is ground, mixed with NaCl and roasted: the copper sulphide is thus converted, first into sulphate by roasting, and then into chloride by double decomposition with the salt. The copper chloride is leached out and the copper is precipitated by iron.

The crude *blister copper* or *precipitate copper* obtained by the above processes is now largely *refined by electrolysis*. For this purpose the metal is cast into plates which are suspended in a bath of copper sulphate solution, acid with H_2SO_4, and are made the anodes, the cathodes being thin sheets of pure copper. When a current (0.2 volt pressure) is passed through the solution from a dynamo, the anodes dissolve and the copper is deposited on the cathodes.

* The ore is exposed in heaps, kept constantly moist.

The copper refined in this manner is almost chemically pure, but requires remelting before being hammered or rolled, on account of the crystalline condition in which it is deposited. In this process the gold, silver, and other metals (except iron, which passes into solution), which may be present in the blister copper, remain in the tanks in the form of a fine mud.

274. For the purpose of illustration, copper may be extracted from copper pyrites on the small scale in the following manner :

200 grains of the powdered ore are mixed with an equal weight of dried borax, and fused in a covered earthen crucible (of about 8 oz. capacity), at a full red heat for about half an hour. The earthy matters associated with the ore are dissolved by the borax, and the pure copper pyrites collects at the bottom of the crucible. The contents of the latter are poured into an iron mould (scorifying mould, Fig. 239), and when the mass has set, it is dipped into water. The semi-mettalic button is then easily detached from the slag by a gentle blow ; it is weighed, finely powdered in an iron mortar, and introduced into an earthen crucible, which is placed obliquely over a dull fire, so that it may not become hot enough to fuse the ore, which should be stirred occasionally with an iron rod to promote the oxidation of the sulphur by the air. When the odour of SO_2 is no longer perceptible, the crucible is placed in a Fletcher's injector furnace (Fig. 225), and exposed for a few minutes to a bright red heat, in order to decompose the sulphates of iron and copper. When no more white fumes of SO_3 are perceived, the crucible is lifted from the furnace, held over the iron mortar, and the roasted ore quickly scraped out of it with a steel spatula. This mixture of the oxides of copper and iron is reduced to a fine powder, mixed with 600 grains of dried carbonate of soda and 60 grains of powdered charcoal, returned to the same crucible, covered with 200 grains of dried borax, and again heated in the furnace for twenty minutes. The crucible is then allowed to cool, and carefully broken to extract the button of metallic copper, which is weighed to ascertain the amount contained in the original ore.

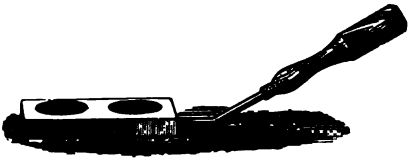


Fig. 239.

275. *Effect of impurities upon the quality of copper.*—The information possessed by chemists upon this subject is still very limited. It has been already mentioned that the presence of a small proportion of *cuprous oxide* in commercial copper is found to increase its toughness. It is believed that copper, perfectly free from metallic impurities, is not improved in quality by the presence of the oxide, but that this substance has the effect of counteracting the red-shortness (see p. 408) of commercial copper, caused by the presence of foreign metals.

Sulphur, even in minute proportion, appears seriously to injure the malleability of copper. *Arsenic* is almost invariably present in copper, very frequently amounting to 0.1 per cent., and does not appear to exercise any injurious influence in this proportion ; indeed, its presence is stated to increase the malleability and tenacity of the metal. *Phosphorus* is not usually found in commercial copper. When purposely added in quantity varying from 0.12 to 0.5 per cent., it increases the hardness and tenacity of the copper, though rendering it somewhat red-short.

Tin, in minute proportion, is also said to increase the toughness of copper, though any considerable proportion renders it brittle. *Antimony* is a very objectionable impurity, and is by no means uncommon in samples of copper. *Nickel* is believed to harden copper in which it occurs. *Bismuth* and *silver* are very generally found in marketable

copper, but their effect upon its quality has not been clearly determined. All impurities appear to affect the malleability and tenacity of copper more perceptibly at high than at low temperatures.

The conducting power of copper for electricity is affected in an extraordinary degree by the presence of impurities. Thus, if the conducting power of chemically pure copper be represented by 100, that of the very pure native copper from Lake Superior has been found to be 93, that of the copper extracted from the malachite of the Burra Burra mines in South Australia was 89, whilst that of Spanish copper, remarkable for containing much arsenic, was only 14.

Copper can be obtained in octahedral crystals. When copper sulphate is heated with a very strong solution of sugar, crystalline copper is deposited.

276. PROPERTIES OF COPPER.—The most prominent character which confers upon copper so high a rank among the useful metals is its malleability, which allows it to be readily fashioned under the hammer, and to be beaten or rolled into thin sheets; among the metals in ordinary use, only gold and silver exceed copper in malleability, and the comparative scarcity of those metals leads to the application of copper for most purposes where great malleability is requisite.

Although, in tenacity or strength, copper ranks high among metals, it is still very far inferior to iron, for a copper wire of $\frac{1}{10}$th inch in diameter will support only 468 lbs., while a similar iron wire will carry 705 lbs. without breaking; and, in consequence of its inferior tenacity, copper is less ductile than iron, and does not admit of being so readily drawn into exceedingly thin wires.

The comparative ease with which copper may be fused allows it to be cast much more readily than iron; for it will be remembered that the latter metal can be liquefied only by the highest attainable furnace heat, whereas copper melts at 1057° C., a temperature generally spoken of as a bright red heat.

As one of the most sonorous of metals, copper has been, from time immemorial, employed in the construction of bells and musical instruments. Its high conductivity for electricity is turned to account in telegraphic communication, its conducting power being almost equal to that of silver, which is the best of electric conductors. In conductivity for heat, copper is surpassed only by silver and gold.

Copper is not so hard as iron, and is somewhat heavier, the specific gravity of cast copper being 8.92, and that of hammered or drawn copper 8.95.

The resistance of copper to the chemical action of moist air gives it a great advantage over iron for many uses, and the circumstance that it does not decompose water in presence of dilute sulphuric acid enables it to be employed as the negative plate in galvanic couples.

Nitric acid is the best solvent for copper, but the presence of nitrous acid seems to be necessary for the attack of the metal (see p. 146). Hydrochloric acid attacks it in presence of oxidising agents.

277. When copper is placed in a solution of salt in water, no perceptible action occurs; but in the course of time, if the air be allowed access, it becomes covered with a green coating of *oxychloride of copper* ($CuCl_2.3CuO.4H_2O$), the action probably consisting, first, in the conversion of the copper into oxide by the air, and afterwards in the decom-

position of the oxide by the sodium chloride; $4CuO + 2NaCl + H_2O = CuCl_2.3CuO + 2NaOH$. The surface of the copper is thus corroded, and in the case of a copper-bottomed ship, the action of sea-water not only occasions a great waste of copper, but roughens the surface of the sheathing, and affords points of attachment to barnacles, &c., which injure the speed of the vessel. Many attempts have been made to obviate this inconvenience. Zinc has been fastened here and there to the outside of the copper, placing the latter in an electro-negative condition; the copper has been coated with various compositions, but with very indifferent success. *Muntz metal*, or *yellow sheathing*, or *malleable brass*, an alloy of 3 parts of copper and 2 parts of zinc, has been employed with some advantage in place of copper, for it is very much cheaper and somewhat less easily corroded; but the difficulty is by no means overcome. Copper containing about 0.5 per cent. of phosphorus is said to be corroded by sea-water much less easily than is pure copper.

278. The use of copper for culinary vessels has occasionally led to serious consequences, from the poisonous nature of its compounds, and from ignorance of the conditions under which these compounds are formed. A perfectly clean surface of metallic copper is not affected by any of the substances employed in the preparation of food, but if the metal has been allowed to remain exposed to the action of the air, it becomes covered with a film of oxide of copper, and this subsequently combines with water and carbonic acid gas derived from the air to produce a basic carbonate of copper,* which, becoming dissolved or mixed with the food prepared in these vessels, confers upon it a poisonous character. This danger may be avoided by the use of vessels which are perfectly clean and bright, but even from these certain articles of food may become contaminated with copper, for this metal is more likely to be oxidised by the air when in contact with acids (vinegar, juices of fruits, &c.), or with fatty matters, or even with common salt; and if oxide of copper be once formed, it will be readily dissolved by such substances. Hence it is usual to coat the interior of copper vessels with tin, which is able to resist the action of the air, even in the presence of acids and saline matters.

279. **Alloys of copper.**—Copper forms a greater number of useful alloys than any other metal. Those of copper with tin (gun-metal and bronze) have been already noticed (p. 452). With from one-third to one-half its weight of zinc, copper forms *brass*, much harder than copper, and capable of being hammered into thin leaves as a substitute for gold. The most important alloys of which copper is a predominant constituent are the following:—

Brass—64 copper, 36 zinc (sp. gr. 8.3).
Muntz metal—60 to 64 copper, 40 to 36 zinc (sp. gr. 8.2).
German silver—61 copper, 19.5 zinc, 19.5 nickel.
Aich or Gedge's metal—60 copper, 38.2 zinc, 1.8 iron.
Sterro-metal—55 copper, 42.4 zinc, 2.6 iron.
Bell metal—78 copper, 22 tin.
Speculum metal—66.6 copper, 33.4 tin.
Bronze—85 copper, 10 tin, 5 zinc.
Gun-metal—90.5 copper, 9.5 tin (sp. gr. 8.5).
Bronze coinage—95 copper, 1 zinc, 4 tin.
Aluminium bronze—90 copper, 10 aluminium.

* Often erroneously called *verdigris*, which is really a basic acetate of copper.

Brass is made by melting copper in a crucible, and adding rather more than half its weight of zinc. An alloy containing 32 per cent. of copper and 68 per cent. of zinc would correspond with the formula Zn_2Cu; thus ordinary brass may be regarded as a solidified solution of this compound in copper. A small quantity of tin is added to brass intended for door-plates, which renders the engraving much easier. When it has to be turned or filed, about 2 per cent. of lead is usually added to it, in order to prevent it from adhering to the tools employed. Brass cannot be melted without losing a portion of its zinc in the form of vapour. When exposed to frequent vibration (as in the suspending chains of chandeliers), it suffers an alteration in structure and becomes extremely brittle. The solder used by braziers consists of equal weights of copper and zinc. In order to prevent ornamental brass-work from being tarnished by the action of air, it is either lacquered or bronzed. *Lacquering* consists simply in varnishing the brass with a solution of shellac in spirit, coloured with dragon's blood. *Bronzing* is effected by applying a solution of arsenic or mercury, or platinum, to the surface of the brass. By the action of arsenious oxide dissolved in hydrochloric acid, upon brass, the latter acquires a coating composed of arsenic and copper, which imparts a bronzed appearance, the zinc being dissolved in place of the arsenic, which combines with the copper at the surface. A mixture of corrosive sublimate (mercuric chloride $HgCl_2$) and acetic acid is also sometimes employed, when the mercury is displaced by the zinc, and precipitated upon the surface of the brass, with which it forms a bronze-like amalgam. For bronzing brass instruments, such as theodolites, levels, &c., a solution of chloride of platinum is employed, the zinc of the brass precipitating a very durable film of metallic platinum upon its surface ($PtCl_4 + Zn_2 = Pt + 2ZnCl_2$).

Aich metal is a kind of brass containing iron, and has been employed for cannon, on account of its great strength. At a red heat it is very malleable.

Sterro-metal (στερρός, strong) is another variety of brass containing iron and tin, said to have been discovered accidentally in making brass with the alloy of zinc and iron obtained during the process of making galvanised iron (page 377). It possesses great strength and elasticity, and is used by engineers for the pumps of hydraulic presses.

Aluminium bronze has been already noticed.

A very hard white alloy of 77 parts of Zn, 17 of Sn, and 6 of Cu, has been employed for the bearings of the driving-wheels of locomotives.

Other *bearing alloys* consist of copper, tin, lead alloys (*e.g.*, Cu 76.8, Sn 8.0, Pb 15.0, P 0.2), and of lead, tin antimony, zinc and copper alloys (*e.g.*, *white metals*, such as Pb 40, Sn 45.5, Sb 13, Cu 1.5).

Iron and steel are coated with a closely adherent film of copper, by placing them in contact with metallic zinc in an alkaline solution of oxide of copper, prepared by mixing sulphate of copper with tartrate of potash and soda, and caustic soda. The copper is thus precipitated upon the iron by slow voltaic action, the zinc being the attacked metal. By adding a solution of stannate of soda to the alkaline copper solution, a deposit of bronze may be obtained.

280. **Oxides of copper.**—Two oxides of copper are well known in the separate state, viz., the suboxide, Cu_2O, and the oxide, CuO. Another oxide, Cu_4O, has been obtained in a hydrated state, and there is some evidence of the existence of an acid oxide, CuO_2.

The *black oxide of copper* (*cupric oxide*), CuO, is employed by the chemist in the ultimate analysis of organic substances by combustion, being prepared for this purpose by acting upon copper with nitric acid to convert it into cupric nitrate (p. 92), and heating this to

dull redness in a rough vessel made of sheet copper, when it leaves the black oxide (sp. gr. 6.3); $Cu(NO_3)_2 = 2NO_2 + O + CuO$. At a higher temperature the oxide fuses into a very hard mass; it evolves very little oxygen when strongly heated. Oxide of copper absorbs water easily from the air, but it is not dissolved by water; acids, however, dissolve it, forming the salts of copper, whence the use of oil of vitriol and nitric acid for cleansing the tarnished surface of copper; a blackened coin, for example, immersed in strong nitric acid, and thoroughly washed, becomes as bright as when freshly coined. Silica dissolves oxide of copper at a high temperature, forming cupric silicate, which is taken advantage of in producing a fine green colour in glass.

Red oxide or *suboxide of copper* (*cuprous oxide*), Cu_2O, is found crystallised in regular octahedra, and is formed when copper is heated in air, that portion of the *copper-scale* which is in contact with the air becoming CuO, while that in contact with the metal is Cu_2O. It is made by heating a mixture of 5 parts of the black oxide with 4 parts of copper filings in a closed crucible. It may also be prepared by boiling a solution of cupric sulphate with a solution containing sodium sulphite and sodium carbonate in equal quantities, when the cuprous oxide is precipitated as a reddish-yellow powder, which should be washed, by decantation, with boiled water—

$$2CuSO_4 + 2Na_2CO_3 + Na_2SO_3 = Cu_2O + 3Na_2SO_4 + 2CO_2.$$

Cu_2O is precipitated in minute octahedral crystals when solution of $CuSO_4$ mixed with glucose is boiled with excess of potash.

Cuprous oxide is a feeble base, but its salts are not easily obtained by direct action of acids, for these generally decompose it into metallic copper and cupric oxide, yielding cupric salts. In the moist state it is slowly oxidised by the air. Ammonia dissolves cuprous oxide, forming a solution which is perfectly colourless until it is allowed to come into contact with air, when it assumes a fine blue colour, becoming converted into an ammoniacal solution of cupric oxide. If the blue solution be placed in a stoppered bottle (quite filled with it) with a strip of clean copper, it will gradually become colourless, the cupric oxide being again reduced to cuprous oxide, a portion of the copper being dissolved. When copper filings are shaken with ammonia in a bottle of air, the same blue solution is obtained (compare p. 86). If the blue solution be poured into a large quantity of water, a light blue precipitate of cupric hydroxide is obtained. The ammoniacal solution of cupric oxide has the unusual property of dissolving paper, cotton, tow, and other varieties of *cellulose*, this substance being reprecipitated from the solution on adding an acid.

Cuprous oxide, added to glass, imparts to it a fine red colour, which is turned to account by the glass-maker.

Quadrant oxide of copper, Cu_4O, has been obtained in combination with water, by the action of stannous chloride and potash upon a cupric salt.

Cuprous hydride, Cu_2H_2, is precipitated when cupric sulphate is heated with hypophosphorous acid; or a strong solution of cupric sulphate may be strongly acidified with dilute sulphuric acid, solution of sodium hypophosphite added, and heated till a brown precipitate forms; this is the hydride, which must not be further heated, as it is decomposed into its elements at 60° C. HCl dissolves it easily, with brisk effervescence from escape of H, and formation of a colourless solution of cuprous chloride, $Cu_2H_2 + 2HCl = Cu_2Cl_2 + 2H_2$.

Cuprous hydrate, $4Cu_2O.H_2O$, is obtained as a yellow precipitate when a solution

of a cuprous salt is added to excess of KOH. If air be excluded, it may be dried at 100° C. without decomposition. Air oxidises it to cupric hydrate. With NH_3 it behaves like cuprous oxide.

Cupric hydroxide, $Cu(OH)_2$, is obtained as a blue precipitate when potash or soda is added to a cupric salt. When boiled in the liquid, it becomes black CuO, but if it be allowed to dry over sulphuric acid, it may be heated to 100° C. without decomposition. Its solubility in ammonia and the properties of the solution have been noticed above. In the presence of tartaric acid, sugar, and many other organic substances, cupric hydroxide dissolves in caustic potash and soda, forming dark blue solutions. The paint known as *blue verditer* is cupric hydroxide obtained by decomposing cupric nitrate with calcium hydroxide.

Cupric acid is believed to be formed when metallic copper is fused with nitre and caustic potash, and when $Cu(OH)_2$ is digested with H_2O_2. The mass from the former reaction yields a blue solution containing K_2CuO_4 in water, which is very easily decomposed with evolution of oxygen and precipitation of cupric oxide. By adding KOH and Br to a solution containing copper a black precipitate, believed to be CuO_2, is formed even in very dilute solutions. The existence of an unstable oxide of copper, containing more than one atom of oxygen, is also rendered probable by the circumstance that oxide of copper acts like manganese dioxide in facilitating the disengagement of oxygen from potassium chlorate by heat (page 41).

Cuprous nitride, Cu_6N_2, is formed by passing ammonia over precipitated CuO at 250° C. It is a dark green powder which decomposes at a high temperature, *evolving* heat.

Cupric nitrate, $Cu(NO_3)_2.3Aq$, crystallises in blue prisms from a solution of copper in nitric acid. It is deliquescent and soluble in water and alcohol. When heated to 65° C., it becomes a green *basic nitrate*, $Cu(NO_3)_2.3Cu(OH)_2$. Cupric nitrate is used as an oxidising-agent in dyeing and calico-printing. Cupric ammonio-nitrate, $Cu(NO_3)_2.4NH_3$, is deposited in dark blue crystals from a mixture of cupric nitrate with excess of ammonia.

281. **Cupric sulphate.**—The beautiful prismatic crystals known as *blue vitriol*, *blue stone*, *blue copperas*, or *sulphate of copper*, have been already mentioned as formed from the residue in the preparation of SO_2 (p. 218), by dissolving copper in oil of vitriol, a process occasionally used for the manufacture of this salt.

The sulphate of copper is also manufactured by roasting copper pyrites ($Cu_2Fe_2S_4$) with free access of air, when it becomes partly converted into a mixture of cupric sulphate with ferrous sulphate: $Cu_2Fe_2S_4 + O_{16} = 2FeSO_4 + 2CuSO_4$. The ferrous sulphate, however, is decomposed by the heat, leaving ferric oxide (see p. 234). When the roasted mass is treated with water, the ferric oxide is left undissolved, but the cupric sulphate, which withstands a higher temperature than ferrous sulphate does, enters into solution, and may be obtained in crystals by evaporation.

Since ferrous sulphate and cupric sulphate are isomorphous, they crystallise together (*v.i.*), and can be separated only by converting the ferrous into ferric sulphate by an oxidising-agent such as nitric acid.

The crystals, as they are found in commerce, are usually opaque, but if they are dissolved in hot water and allowed to crystallise slowly, they become perfectly transparent, and have then the composition expressed by the formula $CuSO_4.5H_2O$ (sp. gr. 2.28). If the crystals be heated to the temperature of boiling water, they lose four-fifths of their water, and crumble down to a greyish-white powder, which has the composition $CuSO_4.H_2O$, and if this be moistened with water, it becomes very hot, and resumes its original blue colour. The whitish opacity of the ordinary crystals of blue stone is due to the absence of a portion of the water of crystallisation. The fifth molecule of water can be expelled

only at a temperature of nearly 200° C., and is therefore generally called water of constitution (see p. 53), the formula of the crystals being then written $CuSO_4.H_2O.4Aq$. The crystals dissolve in 2.5 parts of cold and 0.5 part of boiling water. The solution reddens litmus.

The sulphate of copper is largely employed by the dyer and calico-printer, and in the manufacture of pigments. It is also occasionally used in medicine, in the electrotype process, and in galvanic batteries. In agriculture it is found useful as a preservative, wheat which is to be sown being steeped in a solution of it to protect the grain from the attack of *smut*.

When ammonia is added to solution of cupric sulphate, a basic sulphate is first precipitated, which is dissolved by an excess of ammonia to a dark blue liquid. On allowing this to evaporate, dark blue crystals of *ammonio-cupric sulphate*, $CuSO_4.4NH_3.H_2O$, are deposited. They lose their ammonia when exposed to the air.

A *basic cupric sulphate*, $CuSO_4.3Cu(OH)_2.Aq$, is found as *brochantite*.

Sulphate of copper cannot easily be separated by crystallisation from the sulphates of iron, zinc, and magnesium, because it forms double salts with them, which contain, like those sulphates, seven molecules of water, and are isomorphous with magnesium sulphate (unless the $CuSO_4$ is the predominant constituent, when the salts contain five molecules of water and are isomorphous with cupric sulphate). An instance of this is seen in the *black vitriol* obtained from the mother-liquor of the sulphate of copper at Mansfield, and forming bluish-black crystals isomorphous with green vitriol, $FeSO_4,7H_2O$. The formula of black vitriol may be written $[CuMgFeMnCoNi]SO_4.7H_2O$, the six isomorphous metals being interchangeable without altering the general character of the salt.

Cupric arsenite (*Scheele's green*), $CuHAsO_3$, has been noticed at p. 270. It is a yellowish-green powder, insoluble in water, but easily soluble in acids and alkalies. Its solution in potash has a dark blue colour, and deposits cuprous oxide when boiled, potassium arsenate being produced. *Emerald green* has also been noticed (p. 271).

The basic *cupric phosphates* compose the minerals *tagilite* and *libethenite*.

The basic *cupric carbonates* have been noticed as forming the very beautiful mineral *blue malachite*, *azurite*, or *chessylite*, and *green malachite*.

Mineral green, $CuCO_3.Cu(OH)_2$, has the same composition as green malachite, and is prepared by mixing hot solutions of sodium carbonate and cupric sulphate. When boiled in the liquid, it is gradually converted into black oxide of copper. The green deposit formed on old copper by exposure to air has the same composition.

The blue precipitate produced in cupric solutions by alkaline carbonates in the cold is $CuCO_3.Cu(OH)_2.Aq$.

Cupric silicates are found in the minerals *dioptase*, or *emerald copper*, and *chrysocolla*, $CuH_2SiO_4.H_2O$.

282. **Chlorides of copper.**—The chloride of copper (*cupric chloride*), $CuCl_2$, is produced by the direct union of its elements, when it forms a brown mass, which fuses easily, and is decomposed into chlorine and cuprous chloride, the latter being afterwards converted into vapour. When dissolved in water, it gives a solution which is green when concentrated, and becomes blue on dilution. The hydrated cupric chloride is readily prepared by dissolving the black oxide in hot hydrochloric acid, and allowing the solution to crystallise; it forms green needle-like crystals ($CuCl_2.2H_2O$) which become blue when dried *in vacuo*. A solution of chloride of copper in alcohol burns with a splendid green flame, and the chloride imparts a similar colour to a gas flame.

Oxychloride of copper ($CuCl_2.3CuO.4H_2O$) is found at Atacama in prismatic crystals, and is called *atacamite*. The paint *Brunswick green* has the same composition, and is made by moistening copper with solution of hydrochloric acid or sal-ammoniac, and exposing it to the

air in order that it may absorb oxygen; $Cu_4 + 2HCl + 3H_2O + O_4 = CuCl_2.3CuO.4H_2O$. It is also made by boiling cupric sulphate with chloride of lime. The Brunswick green of the shops frequently consists of a mixture of Prussian blue, chromate of lead, and barium sulphate.

Subchloride of copper (*cuprous chloride*), Cu_2Cl_2, is formed as a sublimate when copper is heated in HCl gas. It is also produced when fine copper turnings are shaken with strong hydrochloric acid in a bottle of air; $Cu_2 + 2HCl + O = Cu_2Cl_2 + H_2O$. The cuprous chloride dissolves in the excess of hydrochloric acid, forming a brown solution, from which water precipitates it *white*, for this is one of the few chlorides insoluble in water. When exposed to light, it assumes a purplish-grey tint. A copper plate dipped into a strong neutral solution of cupric chloride acquires a thin coating of cuprous chloride upon which photographs may be taken. Cuprous chloride may be prepared as described on p. 140.

If the solution in HCl be moderately diluted and set aside, it deposits tetrahedral crystals of cuprous chloride. Ammonia (free from air) dissolves cuprous chloride to a colourless liquid which becomes dark blue by contact with air, absorbing oxygen; it is used as a test for acetylene (p. 140). The solution may be preserved in a colourless state by keeping it in a well-stoppered bottle, quite full, with strips of clean copper. When copper, in a finely divided state, is boiled with solution of ammonium chloride, the solution deposits colourless crystals of the salt, $Cu_2Cl_2(NH_3)_2$. If the solution of this salt be exposed to the air, blue crystals are deposited, having the formula $Cu_2Cl_2.CuCl_2.4NH_3.H_2O$, and on further exposure, a compound of this last salt with ammonium chloride is deposited. The solution of cuprous chloride in hydrochloric acid is employed for absorbing carbonic oxide in the analysis of gaseous mixtures. When this solution is exposed to air it absorbs oxygen, and deposits cupric oxychloride. A strong solution of ammonium or sodium or potassium chloride readily dissolves the cuprous chloride, even in the cold, forming soluble double chlorides, such as $Cu_2Cl_2.4KCl$. The solution in potassium chloride does not absorb oxygen quite so easily as that in ammonium chloride.

Cuprous iodide, Cu_2I_2, is a very insoluble white precipitate formed when a mixture of cupric and ferrous sulphates is added to the solution of an iodide: $2CuSO_4 + 2FeSO_4 + 2KI = Cu_2I_2 + Fe_2(SO_4)_3 + K_2SO_4$. It is also precipitated, together with iodine, when cupric sulphate is added to an iodide; $2CuSO_4 + 4KI = Cu_2I_2 + I_2 + 2K_2SO_4$.

283. **Sulphides of copper.**—Copper has a very marked attraction for sulphur, even at the ordinary temperature. A bright surface of copper soon becomes tarnished by contact with sulphur, and hydrosulphuric acid blackens the metal. Finely divided copper and sulphur combine slowly at the ordinary temperature, and, when heated together, they combine with combustion. A thick copper wire burns easily in vapour of sulphur (p. 212). Copper is even partly converted into sulphides when boiled with sulphuric acid, as in the preparation of sulphurous acid gas. This great attraction of copper for sulphur is taken advantage of in the process of *kernel roasting* for extracting the copper from pyrites containing as little as 1 per cent. of the metal. The pyrites is roasted in large heaps (p. 209) for several weeks, when a great part of the iron is converted into peroxide, and the copper remains combined with sulphur, forming a hard kernel in the centre of the lumps of ore. This kernel contains about 5 per cent. of copper, and can be smelted with economy. Children are employed to detach the kernel from the shell, which consists of ferric oxide mixed with a little cupric sulphate, which is washed out with water.

The *subsulphide of copper*, or *cuprous sulphide* (Cu_2S), has been mentioned among the ores of copper and among the furnace products in smelting, when it is sometimes obtained in octahedral crystals. It is formed when H_2S is passed over red-hot CuO, and when coal-gas is passed over red-hot CuS. It is not attacked by hydrochloric acid, but nitric acid dissolves it readily. *Copper pyrites* is believed to contain the copper in the form of cuprous sulphide, its true formula being $Cu_2S.Fe_2S_3$;* for if the copper be present as cupric sulphide, CuS, the iron must be present as ferrous sulphide, and the mineral would have the formula CuS.FeS. Now, FeS is easily attacked by dilute sulphuric or hydrochloric acid, which is not the case with copper pyrites. Nitric acid, however, attacks it violently.

Sulphide of copper, or *cupric sulphide* (CuS), occurs in nature as *indigo copper* or *blue copper*, and may be obtained as a black precipitate by the action of hydrosulphuric acid upon solution of cupric sulphate. When this precipitate is boiled with sulphur and ammonium sulphide, it is dissolved in small quantity, and the solution on cooling deposits fine scarlet needles containing a higher sulphide of copper combined with sulphide of ammonium. When copper and sulphur are heated together in atomic proportions to a temperature below the boiling-point of sulphur (448° C.), CuS is produced; but at a higher temperature this is converted into Cu_2S. *Pentasulphide of copper* (CuS_5) is obtained by decomposing cupric sulphate with potassium pentasulphide; it forms a black precipitate distinguished from the other sulphides of copper by its solubility in potassium carbonate. The sulphides of copper, when exposed to air in the presence of water, are slowly oxidised and converted into cupric sulphate, which is dissolved by the water. It appears to be in this way that the *blue water* of the copper mines is formed. By thoroughly washing CuS with dil. H_2SO_4 and then with water, it can be made to pass into solution, but it is immediately precipitated by saline matter.

Phosphide of copper, cupric phosphide (Cu_3P_2), obtained as a black powder by boiling solution of cupric sulphate with phosphorus, or by passing PH_3 into a solution of $CuSO_4$, has been already mentioned as a convenient source of phosphine. Another phosphide, obtained by passing vapour of phosphorus over finely divided copper at a high temperature, is employed in Abel's composition for magneto-electric fuses, in conjunction with Cu_2S and $KClO_3$. Phosphide of copper employed for toughening commercial copper is made by running melted copper into a conical iron crucible lined with loam, at the bottom of which are placed sticks of phosphorus which have been coated with copper by soaking them in cold solution of $CuSO_4$.

Silicon may be made to unite with copper by strongly heating finely divided copper with silica and charcoal. A bronze-like mass is thus obtained containing about 5 per cent. Si. It is said to rival iron in ductility and tenacity, and fuses at about the same temperature as bronze.

SILVER.

Ag′ = 107.1 parts by weight.

284. In silver we meet with the first metal hitherto considered which is not capable of undergoing oxidation in the air, and this, in conjunction with its beautiful appearance, occasions its manifold ornamental

* Crystals of $Cu_2S.Fe_2S_3$ are obtained by shaking faintly ammoniacal Cu_2Cl_2 solution with $K_2S.Fe_2S_3$.

uses, which are much favoured also by the great malleability and ductility of this metal (in which it ranks only second to gold), for the former property enables it to be rolled out into thin plates or leaves, so that a small quantity of silver suffices to cover a large surface, whilst its ductility permits the wire-drawer to produce that extremely thin silver wire which is employed in the manufacture of silver lace.

Silver, although pretty widely diffused, is found in comparatively small quantity, and hence it bears a high value, which adapts it for a medium of currency.

As might be expected from its want of direct attraction for oxygen, silver is found frequently in the metallic or native state, crystallised in cubes or octahedra, which are sometimes aggregated together, as in the silver-mines of Potosi, into arborescent or *dendritic* forms; it generally contains copper and gold, and sometimes mercury. Silver is more frequently met with, however, in combination with sulphur, forming the sulphide of silver (Ag_2S), which is generally associated with large quantities of the sulphides of lead, antimony, and iron. The largest supplies of silver are obtained from the United States, Mexican, Peruvian, and Australian (Broken Hill) mines, but the quantity furnished by Saxony and Hungary is by no means insignificant. Silver chloride is found in considerable quantity in the spongy deposits of silica round the Great Salt Lake in Utah.

The process by which silver is extracted from galena has been already described under the history of lead. Silver may be separated from copper, in the ores of which (particularly grey copper ore) it frequently exists to a considerable extent, by taking advantage of the facility with which the former metal is dissolved by melted lead. The process of *liquation*, as it is termed, consists in fusing the argentiferous copper with about thrice its weight of lead, and casting the alloy thus obtained into cakes or discs, which are afterwards gradually heated upon a hearth, so contrived that the lead, which melts much more easily than the copper, may flow off in the liquid state, carrying with it, in the form of an alloy, the silver which was associated with the copper, leaving this last metal in porous masses, having the form of the original discs, upon the hearth. The lead and silver are separated by the process of cupellation (p. 464).

In the extraction of silver from its ores the method adopted depends upon the conditions at the locality where the ore is mined. Thus, where fuel is available it is customary to smelt the ore either with lead ores or copper ores, the noble metal being eventually obtained either in solution in lead or in a copper matte. In the latter case the silver may be extracted by taking advantage of the fact that by carefully roasting a mixture of the sulphides of copper and silver the copper may be completely oxidised to oxide and the silver to sulphate, so that when the roasted mass is leached with water, silver sulphate passes into solution; the metal is precipitated from this by introducing metallic copper, and the precipitate is refined by roasting it to oxidise the impurities, and fusing it. Dissolution in lead followed by cupellation frequently forms a convenient method for refining silver, but electrolytic refining of the metal on the same lines as those adopted for copper (p. 478) is becoming general; the electrolyte is a dilute solution of silver

nitrate, the crude silver cast into plates forms the anode, while sheets of pure silver constitute the cathodes.

Where fuel is scarce an *amalgamation* process is adopted. That in vogue in Mexico is complicated in its chemical details, but primarily depends upon the reduction of the silver from the form of chloride by means of mercury (iron being sometimes substituted as a reducing-agent), $AgCl + Hg = HgCl + Ag$, and the dissolution of the reduced silver in mercury, which is subsequently distilled, leaving the silver to be refined as described above.

The crushed ore is made into a mud with water, and mixed with common salt, mercury, and roasted copper pyrites (*magistral*), the mixing being generally performed by the feet of mules. A hot solution of $CuSO_4$ and more mercury are then added, and after these have been well mixed with the charge the whole is stirred up with water, when the heavy silver amalgam sinks to the bottom. It is drawn off and filtered through canvas, in order to separate the semi-solid amalgam from the excess of mercury. The amalgam is then distilled, the arrangement shown in Fig. 240 being often employed; in this the amalgam is spread on iron trays arranged on an upright beneath an iron bell, the lower part of which stands in water, whilst the upper portion is surrounded by burning fuel, the heat of which distils the mercury into the water.

It would appear that in this process the $CuSO_4$ (which is added both as such and in the form of magistral) reacts with the common salt, yielding cupric chloride. The $CuCl_2$ then reacts with the silver sulphide of the ore, yielding silver chloride, which is dissolved by the solution of salt and reduced by the mercury. The excess of mercury then amalgamates with the silver.

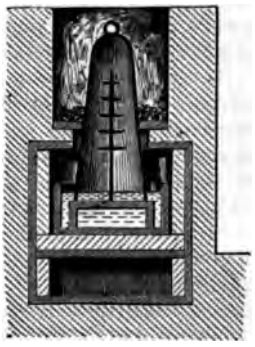


Fig. 240.

In another class of processes for extracting silver from its ores, these are roasted with common salt, whereby the silver sulphide is first converted into sulphate by oxidation, and then into chloride by double decomposition with the NaCl. The silver chloride is dissolved out of the mass by means of a strong solution of common salt, from which the silver is afterwards precipitated in the metallic state by copper, or as silver iodide, the silver iodide being reduced by zinc, and the zinc iodide used to precipitate a fresh portion of silver. Sodium thiosulphate is also employed to dissolve out the silver chloride, and the solution precipitated by sodium sulphide, the silver sulphide thus obtained being roasted to remove the sulphur and leave metallic silver.

Although silver is capable of resisting the oxidising action of the atmosphere, it is liable to considerable loss by wear and tear, in consequence of its softness, and is therefore always hardened, for useful purposes, by the addition of a small proportion of copper. The *standard silver* employed for coinage and for most articles of silver plate in this country, contains, in 1000 parts, 925 of silver and 75 of copper, whilst that used in France contains 900 of silver and 100 of copper. English standard silver is said to have a *fineness* of 925, and French, of 900.

Standard silver, for coining and other purposes, is whitened by being heated in air and immersed in diluted sulphuric acid, which dissolves out the oxide of copper, leaving a superficial film of nearly pure silver. *Dead* or *frosted* silver is produced in this manner. *Oxidised* silver is

covered with a thin film of sulphide by immersion in a solution obtained by boiling sulphur with potash.

The solder employed in working silver consists of 5 parts of silver, 2 of zinc, and 6 of brass.

Plated articles are manufactured from copper or one of its alloys, which has been united, by rolling, with a thin plate of silver, the adhesion of the latter being promoted by first washing the surface of the copper with a solution of silver nitrate, when a film of this metal is deposited upon its surface, the copper taking the place of the silver in the solution.

Electro-plating consists in covering the surface of baser metals with a coating of silver, by connecting them with the negative (or zinc) pole of the galvanic battery, and immersing them in a solution made by dissolving silver cyanide in potassium cyanide,* the positive (copper or platinum) pole being connected with a silver plate, also immersed in the solution; the current gradually decomposes the silver cyanide, and this metal is of course (see p. 324) deposited upon the object connected with the negative electrode, whilst the cyanogen liberated at the silver plate attacks the silver, so that the solution is always maintained at the same strength, the quantity of silver dissolved at this electrode being precisely equal to that deposited at the opposite one.

Brass and copper are sometimes silvered by rubbing them with a mixture of 10 parts of silver chloride with 1 of corrosive sublimate (mercuric chloride) and 100 of bitartrate of potash. The silver and mercury are both reduced to the metallic state by the baser metal, and an amalgam of silver is formed, which readily coats the surface. The acidity of the bitartrate of potash promotes the reduction. The surface to be silvered should always be cleansed from oxide by momentary immersion in nitric acid, and washed with water. For *dry silvering*, an amalgam of silver and mercury is applied to the clean surface, and the mercury is afterwards expelled by heat.

Silvering upon glass is effected by means of certain organic substances which are capable of precipitating metallic silver from its solutions. Looking-glasses have been made by pouring upon the surface of plates of glass a solution containing silver tartrate and ammonium tartrate. On heating the glass plates to a certain temperature the tartrate is reduced, and the metallic silver is deposited in a closely adhering film. Glass globes and vases are silvered internally by a process which is exactly similar in principle. The coating is rendered more adherent by sprinkling it with a weak solution of potassio-mercuric cyanide, which amalgamates the silver.

Small surfaces of glass for optical purposes may be silvered in the following manner: Dissolve one gram of $AgNO_3$ in 20 c.c. of distilled water, and add weak NH_3 carefully until the precipitate is almost entirely dissolved. Filter the solution and make it up to 100 c.c. with distilled water. Then dissolve 2 grams of $AgNO_3$ in a little distilled water, and add it to a litre of boiling distilled water. Add 1.66 gram of Rochelle salt (tartrate of potassium and sodium), and boil till the precipitated silver tartrate becomes grey; filter while hot. Clean the glass to be silvered *very thoroughly* with HNO_3, distilled water, KOH, distilled water, alcohol, distilled water; place it in a *clean* glass or porcelain vessel, with the side to be silvered uppermost. Mix equal measures of the two silver solutions (cold), and

* A solution of potassium cyanide in 10 parts of water, with 50 grains of silver chloride dissolved in each pint of the liquid, will answer the purpose.

pour the mixture in so as to cover the glass, which will be silvered in about an hour. After washing, it may be allowed to dry, and varnished.

Very good mirrors may be made by adding ammonia to weak silver nitrate till the precipitate just redissolves, then a little potash, then ammonia till the liquid is clear, and then a very little glycerine. If a watch-glass be floated on this liquid, and a gentle heat applied, a good mirror will be formed in a few minutes.

Pure silver is easily obtained from standard silver by dissolving it in nitric acid, with the aid of heat, diluting the solution with water, adding solution of common salt as long as it produces any fresh precipitate of silver chloride, washing the precipitate by decantation as long as the washings give a blue tinge with ammonia, and fusing the dried precipitate with half its weight of dried sodium carbonate in a brisk fire, when a button of silver will be found on breaking the crucible—

$$2AgCl + Na_2CO_3 = Ag_2 + 2NaCl + O + CO_2.$$

The pure silver employed by Stas in his researches on atomic weights was prepared by distilling the metal.

When fused in air, silver occludes oxygen, a portion of which it evolves during solidification, causing *sprouting* on the surface of the partly solidified metal, and sometimes projection of portions of the mass. After cooling, it still retains oxygen, which can only be expelled by heating to about 600° C. in a vacuum. This may amount to 0.025 per cent. by weight, and has to be taken into consideration in determining atomic weights in terms of silver.*

285. **Properties of silver.**—The brilliant whiteness of silver distinguishes it from all other metals. It is lighter than lead, its specific gravity being 10.53; harder than gold, but not so hard as copper; more malleable and ductile than any other metal except gold, which it surpasses in tenacity. It fuses at a somewhat lower temperature than gold or copper (960° C.), and is the best conductor of heat and electricity. It is comparatively easily distilled. It is not oxidised by dry or moist air, either at the ordinary or at high temperatures, but is oxidised by ozone, and tarnished by air containing sulphuretted hydrogen, from the production of silver sulphide, which is easily removed by solution of potassium cyanide. Pure H_2S does not attack silver. It is unaffected by dilute acids, with the exception of nitric, and in this case the presence of nitrous acid is essential; but hot concentrated sulphuric acid converts it into silver sulphate, and when boiled with strong hydrochloric acid it dissolves to a slight extent in the form of silver chloride, which is precipitated on adding water. Strong hydriodic acid dissolves silver, evolving hydrogen; silver iodide is precipitated on addition of water. The alkali hydroxides do not act on silver to the same extent as on platinum when fused with it; hence silver basins and crucibles are much used in the laboratory.

Colloidal silver appears to be formed by the action of certain reducing-agents on a solution of silver nitrate, and has lately been applied in medicine. When a solution of ferrous citrate is added to one of silver nitrate, a red solution which deposits a lilac precipitate is obtained; this precipitate is washed with ammonium nitrate solution, and is then found to contain over 97 per cent. of silver, and to be soluble in water to a red solution. By similar methods an *insoluble allotropic silver* and an insoluble *gold-like allotropic silver* have been obtained. The physical properties of silver deposited as a mirror seem to show that it is colloidal silver.

* At 300° C. and 15 atmospheres pressure Ag absorbs as much oxygen as corresponds with the formula Ag_4O.

286. **Oxides of silver.**—There are three compounds of silver with oxygen—the suboxide, Ag_4O; the oxide Ag_2O; and the peroxide, probably Ag_2O_2, which is not known in the pure state. The oxide alone has any practical interest, as being the base of the salts of silver.

Silver oxide (Ag_2O) is obtained as a brown precipitate when solution of silver nitrate is decomposed by potash, or, better, poured into an excess of lime-water. When alcoholic solutions of KOH and $AgNO_3$ are mixed at -40° C. a white precipitate of *silver hydroxide*, AgOH, is produced; as the temperature rises, however, it becomes dark from loss of water and formation of Ag_2O. The oxide is a powerful base, slightly soluble in water, to which it imparts a weak alkaline reaction. A temperature of 270° C. decomposes it into its elements. It acts as a powerful oxidising-agent. When moist freshly precipitated silver oxide is covered with a strong solution of ammonia, and allowed to stand for some hours, it becomes black, crystalline, and acquires dangerously explosive properties. The composition of this *fulminating silver* is not accurately known, but it is supposed to be a silver nitride, NAg_3, corresponding in composition with ammonia.

Silver peroxide is a black precipitate obtained by mixing solutions of potassium persulphate and $AgNO_3$. With ammonium persulphate there is less precipitate, and if NH_3 be present there is a violent evolution of nitrogen, the silver salt acting catalytically to decompose the mixture in the sense of the equation $3(NH_4)_2S_2O_8 + 8NH_3 = 6(NH_4)_2SO_4 + N_2$. The peroxide is also deposited on the anode during the electrolysis of silver salts as black octahedra which dissolve in HNO_3 to a deep brown solution of strongly oxidising properties.

Silver nitrate ($AgNO_3$), or *lunar caustic* (silver being distinguished as *luna* by the alchemists), is procured by dissolving silver in nitric acid,* with the aid of a gentle heat, evaporating the solution to dryness, and heating the residue till it fuses, in order to expel the excess of acid. It fuses at 218° C. For use in surgery, the fused nitrate is poured into cylindrical moulds, so as to cast it into thin sticks; but for chemical purposes it is dissolved in water and crystallised, when it forms colourless square tables (sp. gr. 4.3), easily soluble in water and alcohol. The action of nitrate of silver as a caustic depends upon the facility with which it parts with oxygen, the silver being reduced to the metallic state, and the oxygen combining with the elements of the organic matter. This effect is very much promoted by exposure to sunlight or diffused daylight. Pure silver nitrate is not changed by exposure to light, but if organic matter be present, a black deposit, containing finely divided silver, is produced. Thus, the solution of silver nitrate stains the fingers black when exposed to light, but the stain may be removed by potassium cyanide or, more safely, by tincture of iodine. If solution of silver nitrate be dropped upon paper and exposed to light, black stains will be produced, and the paper corroded. Silver nitrate is a frequent constituent of marking-inks, since the deposit of metallic silver formed on exposure to light is not removable by washing. The linen is sometimes *mordanted* by applying a solution of sodium carbonate before the marking-ink, when the insoluble silver carbonate is precipitated in the fibre, and is more easily blackened than the nitrate, especially if a hot iron is applied. Marking-inks without preparation, are made with silver nitrate containing an excess of ammonia, which

* For 3 ounces of silver, take $1\frac{3}{4}$ fluid ounce of strong nitric acid, and 5 fluid ounces of water.

appropriates the nitric acid, and hastens the blackening on exposure to light or heat. Hair-dyes often contain $AgNO_3$. The important use of this salt in photography has been noticed already (p. 236).

In order to prepare silver nitrate from standard silver (containing copper), the metal is dissolved in moderately strong nitric acid, and the solution evaporated to dryness in a porcelain dish, when a blue residue containing the nitrates of silver and copper is obtained. The dish is now moderately heated until the residue has fused, and become uniformly black, the blue copper nitrate being decomposed and leaving black copper oxide, at a temperature which is insufficient to decompose the silver nitrate. To ascertain when all the copper nitrate is decomposed, a small sample is removed on the end of a glass rod, dissolved in water, filtered, and tested with ammonia, which will produce a blue colour if any copper nitrate be left. The residue is treated with hot water, the solution filtered from the copper oxide and evaporated to crystallisation.

Silver nitrate forms crystalline double salts with one molecule of potassium or ammonium nitrate. It absorbs ammonia with evolution of heat, and *silver ammonio-nitrate*, $AgNO_3.2NH_3$, may be crystallised from a strong solution of silver nitrate saturated with ammonia.

Silver nitrite, $AgNO_2$, is obtained as a white precipitate from KNO_2 and $AgNO_3$. It is soluble in hot water and crystallises in prisms. By long boiling with water it is decomposed, $2AgNO_2 = AgNO_3 + Ag + NO$. *Silver hyponitrite*, $Ag_2N_2O_2$ (see p. 103).

Silver carbonate, Ag_2CO_3, is obtained in transparent yellow crystals when moist silver oxide is acted on by CO_2. It dissolves in solution of CO_2, like $CaCO_3$, and is deposited in crystals when the solution is exposed to the air. It is feebly alkaline to moist test-paper. It bears heating to nearly the boiling-point of oil, and fuses just before decomposition. Silver carbonate forms a yellowish white precipitate when silver nitrate is decomposed by an alkaline carbonate.

287. **Silver chloride**, AgCl, is an important compound, as being the form into which silver is commonly converted in extracting it from its ores, and in separating it from other metals. It separates, as a white curdy precipitate, when solution of hydrochloric acid or a chloride is mixed with a solution containing silver. The precipitate is brilliantly white at first, but soon becomes violet, and eventually black, if exposed to daylight, or more rapidly in sunlight, the chloride of silver being reduced to subchloride (Ag_2Cl), with separation of chlorine (see p. 236). The blackening is more rapid in the presence of an excess of silver nitrate or of organic matter, upon which the liberated chlorine can act. In the presence of chlorine the blackening does not occur; nor will perfectly dry AgCl darken. If the white silver chloride be dried in the dark and heated in a crucible, it fuses at 457° C. to a brownish liquid, which solidifies, on cooling, to a transparent, nearly colourless mass (sp. gr. 5.59), much resembling horn in external characters (*horn silver*); a strong heat converts it into vapour, but does not decompose it. If fused silver chloride be covered with hydrochloric acid, and a piece of zinc placed upon it, it will be found entirely reduced, after a few hours, to a cake of metallic silver; the first portion of silver having been reduced in contact with the zinc, and the remainder by the galvanic action set up by the contact of the two metals beneath the liquid. Fusion with Na_2CO_3 reduces AgCl, first converting it into Ag_2CO_3 which breaks up into Ag_2, O, and CO_2. Silver chloride is slightly soluble in strong HCl, and in strong solutions of alkali chlorides. Potassium cyanide dissolves it readily, and the solution is used in electro-plating. Ammonia readily dissolves silver chloride, and the solution deposits colourless crystals of the chloride when evaporated. If the ammonia be very strong the solution deposits a crystalline compound of silver chloride

with ammonia, $2AgCl.3NH_3$. The absorption of ammoniacal gas by silver chloride has been noticed at p. 82, and the photographic application of the chloride at p. 236.

From photographic fixing solutions containing sodium hyposulphite the silver cannot be precipitated by salt, because the silver chloride is soluble in the hyposulphite. A piece of sheet copper left in this for a day or two will precipitate the silver at once in the metallic state.

Several chemists have claimed to have isolated a dark *silver sub-chloride*, to which the formulæ Ag_2Cl and Ag_4Cl_2 have been ascribed. The interest in this supposed sub-chloride arises from the fact that metallic silver cannot be found in the silver chloride which has been darkened by light, although chlorine has undoubtedly been removed. By adding a reducing-agent (such as $SnCl_2$) to an ammoniacal solution of AgCl, a black precipitate is obtained, which becomes coloured pink or brown (according to the nature of the reducing-agent) when it is washed with nitric acid. A number of such coloured salts has been obtained by Carey Lea from the halides of silver; these are termed *photo-salts of silver* and are supposed to be identical with the products of the action of light on the silver halides; they appear to consist of the normal silver halides with small admixtures of sub-halides. They are dissolved by ammonia with the exception of a slight residue of silver.

Silver bromide (AgBr) is a rare Chilian mineral, *bromargyrite*. Associated with AgCl it forms the mineral *embolite*. It much resembles the chloride, but is somewhat less easily dissolved by ammonia. Dry silver bromide does not absorb NH_3. It melts at 427° C.; sp. gr. 6.35. When heated to 700° C. in HCl, silver bromide is converted into the chloride, but, at the ordinary temperature, HBr converts silver chloride into bromide. Modern photographic plates are made with silver bromide.

Ammonium bromide is dissolved in a warm aqueous solution of gelatine and a solution of silver nitrate, less than equivalent to the bromide, is poured in, the room being lighted by red light. The mixture, with the finely divided silver bromide suspended in it, is warmed for some time in order to "ripen" the emulsion. By this expression it is implied that the silver bromide becomes more sensitive to light, a fact which has not been explained; the sole effect of the ripening on the silver bromide, so far as has been observed, is the aggregation of the particles, so that they become somewhat coarser. The emulsion is now allowed to set, and washed in water to remove the ammonium nitrate produced by the interaction of the NH_4Br and $AgNO_3$, and the excess of NH_4Br; if the latter be not present during the manufacture of the emulsion a less sensitive plate is produced. The gelatine emulsion is again melted and poured on to the plates.

What has been said (p. 493) with reference to the action of light on AgCl may be applied to AgBr. The chemistry of the action and of the development of the invisible image is even yet shrouded in mystery.

Silver iodide (AgI) is also found in the mineral kingdom. It is worthy of remark that silver decomposes hydriodic acid much more easily than hydrochloric acid, forming silver iodide, and evolving hydrogen. The silver iodide dissolves in hot hydriodic acid, and the solution deposits crystals of AgI.HI, which are decomposed in the air. If the hot solution be left in contract with silver, prisms of AgI are deposited. By adding silver nitrate to potassium iodide, the silver iodide is obtained as a yellow precipitate, which, unlike the chloride, does not dissolve in ammonia, but is bleached, forming $2AgI.NH_3$, which is also produced when dry silver iodide absorbs ammonia.

Silver iodide is remarkable for its behaviour when heated. It becomes more yellow as the temperature rises and melts to an orange liquid at 527° C. The melted mass contracts considerably on solidifying and on cooling, until the temperature is 116° C., whereupon a sudden expansion occurs, concomitant with the passage of the red amorphous to the yellow crystalline modification. When the

molten iodide is poured into cold water it becomes yellow, but remains amorphous. The sp. gr. of the fused iodide is 5.6.

Silver iodide is the most stable of the silver halides ; when exposed to light it requires a more vigorous *sensitising-agent* (*i.e.*, halogen-absorbent) than do the other halides in order that it may undergo *photo-reduction*. It dissolves in a boiling saturated solution of silver nitrate, and the solution, on cooling, deposits crystals having the composition $AgI.AgNO_3$; these are sensitive to light since the halogen-absorbent ($AgNO_3$) is ready to hand. The crystals are decomposed by water with separation of silver iodide.

Silver fluoride, AgF, is deliquescent and very soluble in water, forming crystals which may contain one or two molecules of water. It fuses to a horny mass, like AgCl, but is reduced to the metallic state when heated in moist air. Ammonia also reduces it to the metallic state when heated. Fused AgF conducts the electric current without undergoing decomposition.

Silver sulphide (Ag_2S) is found as *silver glance*, which may be regarded as the chief ore of silver ; it has a metallic lustre, and is sometimes found in cubical or octahedral crystals. The minerals known as *rosiclers* or *red silver ores* contain sulphide of silver combined with the sulphides of arsenic and antimony. The black precipitate obtained by the action of hydrosulphuric acid upon a solution of silver is silver sulphide. It may also be formed by heating silver with sulphur in a covered crucible. Silver sulphide is remarkable for being soft and malleable, so that medals may even be struck from it. It is not dissolved by diluted sulphuric or hydrochloric acid, but nitric acid readily dissolves it. Metallic silver dissolves silver sulphide when fused with it, and becomes brittle even when containing only 1 per cent. of the sulphide. Ag_2S fuses unchanged, but when roasted in air it becomes Ag_2SO_4.

Silver sulphate, Ag_2SO_4, forms a crystalline precipitate when a strong solution of silver nitrate is stirred with dilute sulphuric acid. It requires 200 parts of cold water to dissolve it. It fuses at 654° C. $AgHSO_4$ has been crystallised.

Silver sulphite, Ag_2SO_3, forms a white precipitate when sulphurous acid is added to silver nitrate. Boiling with water reduces it to metallic silver ;

$$Ag_2SO_3 + H_2O = Ag_2 + H_2SO_4.$$

Silver orthophosphate, Ag_3PO_4, forms a yellow precipitate when sodium phosphate is added to silver nitrate (p. 259). It is soluble in nitric acid and in ammonia, and is thus distinguished from silver iodide.

Silver arsenite, Ag_3AsO_3, is obtained as a yellow precipitate when ammonia is cautiously added to a mixture of silver nitrate and arsenious acid ; it is soluble in nitric acid and in ammonia. *Silver arsenate*, Ag_3AsO_4, is a red precipitate, soluble in nitric acid and in ammonia, formed when silver nitrate is added to arsenic acid.

Silver sulpharsenite, Ag_3AsS_3, is found as *light red silver ore*.

Silver sulphantimonate, Ag_3SbS_3, is *dark red silver ore*.

MERCURY.

Hg″ = 199 parts by weight = 2 vols.

288. Mercury (*quicksilver*) is conspicuous among metals by its fluidity, and among liquids by its not wetting or adhering to most solids, such as glass, a property of great value in making philosophical instruments. It is the only metal which is liquid at the ordinary temperature, and since it does not freeze until −39° F. (−39°.5 C.), this metal is particularly adapted for the construction of thermometers and barometers. Its high boiling-point (662° F., 357° C.) and low specific heat (0.033) also recommend it for the former purpose, as its high specific gravity (13.54) does for the latter, a column of about 30 inches in height being able to counterpoise a column of the atmosphere having the same sectional area. The symbol for mercury (Hg) is derived from the Latin name for this element, *hydrargyrum* (*ὕδωρ*, *water*, referring to its fluidity, *ἄργυρος*, *silver*).

Mercury is not met with in this country, but is obtained from Idria

(Austria), Almaden (Spain), China, and New Almaden (California). It occurs in these mines partly in the metallic state, diffused in minute globules or collected in cavities, but chiefly in the state of cinnabar, which is mercuric sulphide, HgS (sp. gr. 8.2).

The metal is extracted from the sulphide at Idria by roasting the ore in a kiln (Fig. 241), which is connected with an extensive series of con-

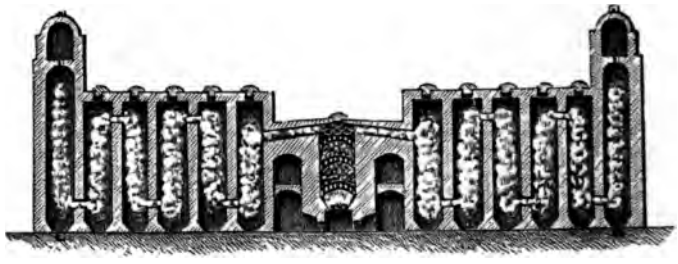


Fig. 241.—Extraction of mercury at Idria.

densing-chambers built of brickwork. The sulphur is converted, by the air in the kiln, into sulphurous acid gas, whilst the mercury passes off in vapour and condenses in the chambers.

At Almaden, the extraction is conducted upon the same principle, but the condensation of the mercury is effected in earthen receivers (called *aludels*) opening into each other, and delivering the mercury into a gutter which conveys it to the receptacles.

The cinnabar is placed upon the arch (A, Fig. 242) of brickwork, in which there are several openings for the passage of the flame of the wood fire kindled at B; this flame ignites the sulphide of mercury, which burns in the air passing up from below, forming sulphurous acid gas and vapour of mercury ($HgS + O_2 = Hg + SO_2$), which escape through the flue (F) into the aludels (C), where the chief part of the mercury condenses and runs down into the gutter (G). The sulphurous acid gas escapes through the flue (H), and any mercury which may have escaped condensation is collected in the trough (D), the gas finally passing out through the chimney (E), which provides for the requisite draught.

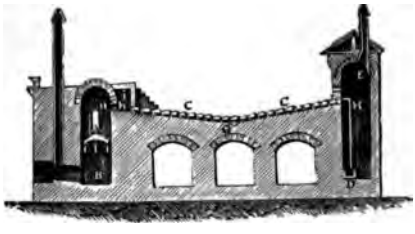


Fig. 242.

In the Palatinate the cinnabar is distilled in cast-iron retorts with lime, when the sulphur is left in the residue as calcium sulphide and sulphate, whilst the mercury distils over—

$$4HgS + 4CaO = 3CaS + CaSO_4 + Hg_4.$$

The mercury found in commerce is never perfectly pure, as may be shown by scattering a little upon a clean glass plate, when it *tails* or leaves a track upon the glass, which is not the case with pure mercury. Its chief impurity is lead, which may be removed by exposing it in a thin layer to the action of nitric acid diluted with two measures of water, which should cover its surface, and be allowed to remain in contact with it for a day or two with occasional stirring. The lead is far more easily oxidised and dissolved than the mercury, though a little of this also passes into solution. The mercury is afterwards well washed with water and

dried, first with blotting-paper, and then by a gentle heat. Mercury is easily freed from mechanical impurities by squeezing it through a duster. Zinc, tin, and bismuth are sometimes present in the mercury of commerce, and may be partly removed, as oxides, by shaking the mercury in a large bottle with a little powdered loaf-sugar for a few minutes, and straining through cloth. The sugar appears to act mechanically by dividing the mercury.

289. In its chemical properties mercury much resembles silver, being unaffected by ordinary air and tarnished by air containing H_2S. In course of time, however, it becomes oxidised, as may be seen in old instruments containing mercury and air; and it is slowly oxidised when heated in air, which is not the case with silver. It also appears to undergo a partial oxidation when reduced to a fine state of division, as in those medicinal preparations of the metal which are made by triturating it with various substances which have no chemical action upon it, until globules of the metal are no longer visible. *Blue pill* and *grey powder*, or *hydrargyrum cum cretâ*, afford examples of this, and probably owe much of their medicinal activity to the presence of one of the oxides of mercury.

Nitric acid (containing nitrous acid) dissolves mercury, and converts it into two nitrates—mercurous, $HgNO_3$, corresponding with $AgNO_3$, and mercuric, $Hg(NO_3)_2$. Hot concentrated sulphuric acid also converts it into mercurous (Hg_2SO_4) and mercuric ($HgSO_4$) sulphates. Mercury is precipitated from solutions of its salts by reducing-agents, stannous chloride, for example, in what looks like a dark grey powder; but if this be boiled in the liquid, the minute globules of which it is composed gradually unite into fluid mercury. Conversely, if mercury be diligently triturated with chalk or grease, it may be divided into extremely minute globules which behave like a powder.

290. **Uses of Mercury.**—One of the chief uses to which mercury is devoted is the *silvering of looking-glasses*, which is effected by means of an amalgam of tin in the following manner: A sheet of tinfoil of the same size as the glass to be silvered is laid perfectly level upon a table, and rubbed over with metallic mercury, a thin layer of which is afterwards poured upon it. The glass is then carefully slid on to the table, so that its edge may carry before it part of the superfluous mercury with the impurities upon its surface; heavy weights are laid upon the glass, so as to squeeze out the excess of mercury, and in a few days the combination of tin and mercury is found to have adhered firmly to the glass; this coating usually contains about 1 part of mercury and 4 parts of tin. In this and all other arts in which mercury is used (such as barometer-making) much suffering is experienced by the operatives, from the poisonous action of the mercury.

The readiness with which mercury unites with most other metals to form *amalgams* is one of its most striking properties, and is turned to account for the extraction of silver and gold from their ores. The attraction of the latter metal for mercury is seen in the readiness with which it becomes coated with a silvery layer of mercury, whenever it is brought in contact with that metal, and if a piece of gold leaf be suspended at a little distance above the surface of mercury, it will be found, after a time, silvered by the vapour of the metal, which rises slowly even at the ordinary temperature. From the surface of rings which have been accidentally whitened by mercury it may be removed by a moderate

heat, or by warm dilute nitric acid, but the gold will afterwards require burnishing.

Zinc plates are *amalgamated*, as already explained (p. 14), for use in the galvanic battery. An amalgam of 6 parts of mercury with 1 part of zinc and 1 of tin is used to promote the action of frictional electrical machines.

The addition of a little amalgam of sodium to metallic mercury gives it the power of adhering much more readily to other metals, even to iron. Such an addition has been recommended in all cases where metallic surfaces have to be amalgamated, and especially in the extraction of silver and gold from their ores by means of mercury. *Gold amalgam* and *cadmium amalgam* are used by dentists. *Sodium amalgam*, in contact with water, forms a convenient source of *nascent* (atomic) hydrogen.

Iron and platinum are the only metals in ordinary use which can be employed in contact with mercury without being corroded by it. Mercury, however, adheres to platinum.

The following definite compounds of mercury with other metals have been obtained by combining them with excess of mercury, and squeezing out the fluid metal by hydraulic pressure, amounting to 60 tons upon the inch; Pb_2Hg, AgHg, FeHg,* Zn_2Hg, CuHg, $PtHg_2$. AgHg has been found in nature, in dodecahedral crystals.

A very beautiful crystallisation of the amalgam of silver (*Arbor Dianæ*) may be obtained in long prisms having the composition Ag_2Hg_3, by dissolving 400 grains of silver nitrate in 40 measured ounces of water, adding 160 minims of concentrated nitric acid, and 1840 grains of mercury; in the course of a day or two crystals of 2 or 3 inches in length will be deposited.

291. **Oxides of Mercury.**—Two oxides of mercury are known—the suboxide, Hg_2O, and the oxide, HgO; both combine with acids to form salts. *Suboxide of mercury*, *black oxide*, or *mercurous oxide*, Hg_2O, is obtained by decomposing calomel with solution of potash, and washing with water; $Hg_2Cl_2 + 2KOH = Hg_2O + 2KCl + H_2O$. It is very easily decomposed, by exposure to light or to a gentle heat, into mercuric oxide and metallic mercury.

Red oxide of mercury, or *mercuric oxide* (HgO), is formed upon the surface of mercury, when heated (237° C) for some time to its boiling-point in contact with air. The oxide is black while hot, but becomes red on cooling. It is used, under the name of *red precipitate*, in ointments, and is prepared for this purpose by dissolving mercury in nitric acid, evaporating the solution to dryness, triturating the mercuric nitrate with an equal weight of mercury, and heating as long as acid fumes are evolved; $Hg(NO_3)_2 + Hg_2 = 3HgO + N_2O_3$. The name *nitric oxide of mercury* refers to this process. It is thus obtained, after cooling, as a brilliant red crystalline powder (sp. gr. 11.0), which becomes nearly black when heated, and is resolved into its elements at a red heat. It dissolves slightly in water, and the solution has a very feeble alkaline reaction. A bright yellow modification of the oxide is precipitated when a solution of corrosive sublimate is decomposed by potash ($HgCl_2 + 2KOH = HgO + 2KCl + H_2O$); the yellow variety is chemically more active than the red.

* Hg_3Fe_2 has been obtained by the action of finely divided iron on sodium amalgam in presence of water.

When mercuric oxide is attacked by strong ammonia it becomes converted into a yellowish-white powder which possesses the properties of a strong base, absorbing carbonic acid eagerly from the air, and combining readily with other acids. It is easily decomposed by exposure to light, and if rubbed in a mortar when dry, is decomposed with slight detonations, a property in which it feebly resembles fulminating silver (p. 492). The composition of this substance is represented by the formula $NHg''_2.OH.Aq$. When exposed *in vacuo* over oil of vitriol, it loses Aq. becoming $NHg''_2.OH$, or *dimercurammonium hydroxide*, which is a brown explosive base.* When treated with aqueous ammonia it yields *Millon's base*, $3(2HgO.NH_3).2H_2O$, which is not decomposed by boiling potash, but explodes if evaporated to dryness with the potash. This base will deprive all soluble and most insoluble salts of their acids; thus it will remove sulphates and chlorides from impure soda solution.

By passing ammonia gas over the yellow oxide of mercury as long as it is absorbed, and heating the compound to about 127° C. in a current of ammonia as long as any water is evolved, a brown explosive powder is obtained which is believed to be a *nitride of mercury*, $N_2Hg''_3$, representing a double molecule of ammonia in which the hydrogen has been displaced by mercury. It yields salts of ammonium when decomposed by acids.

292. The salts formed by the oxides of mercury with the oxygen-acids are not of great practical importance. *Protonitrate of mercury*, or *mercurous nitrate*, $Hg(NO_3)Aq$, is obtained when mercury is dissolved in cold HNO_3 diluted with five volumes of water. The prismatic crystals which are sometimes sold as protonitrate of mercury consist of a basic nitrate, $Hg_4(NO_3)_2OH$, prepared by acting with dilute nitric acid upon mercury in excess. When this salt is powdered in a mortar with a little common salt, it becomes black from the separation of mercurous oxide—$2Hg_4(NO_3)_2OH + 6NaCl = 6NaNO_3 + 6HgCl + Hg_2O + H_2O$; but the normal nitrate is not blackened $(Hg(NO_3) + NaCl = HgCl + NaNO_3)$. Mercurous nitrate is soluble in a little hot water, but much water decomposes it into nitric acid and a basic nitrate; $2Hg(NO_3) + H_2O = Hg_2NO_3.OH + HNO_3$.

Nitrate of mercury or *mercuric nitrate*, $2Hg(NO_3)_2.Aq$, is formed when mercury is dissolved in an excess of strong nitric acid, and the solution boiled until it is no longer precipitated by NaCl. Water decomposes it, precipitating a yellow basic nitrate, which leaves mercuric oxide when long washed with water. Mercuric nitrate stains the skin red. When nitric acid is heated with an excess of mercuric oxide, the solution, on cooling, deposits crystals of a *basic mercuric nitrate*; $Hg_3(NO_3)_2.OH.Aq$.

Mercurous sulphate (Hg_2SO_4) is precipitated as a white crystalline powder when dilute sulphuric acid is added to a solution of mercurous nitrate.

Mercuric sulphate ($HgSO_4$) is obtained by heating 2 parts by weight of mercury with 3 parts of oil of vitriol, and evaporating to dryness. Mercurous sulphate is first produced, and is oxidised by the excess of sulphuric acid. It forms a white crystalline powder, which becomes brown-yellow when heated, and white again on cooling. It is decomposed by water into a soluble acid sulphate, and an insoluble yellow basic sulphate of mercury, $HgSO_4.2HgO$, known as *turbith* or *turpeth* mineral, said to have been so named from its resembling in its medicinal effects the root of the *Convolvulus turpethum*.

293. **Chlorides of Mercury.**—The chlorides are the most important of the compounds of mercury, one chloride being *calomel* ($HgCl$) and the other *corrosive sublimate* ($HgCl_2$). Vapour of mercury burns in chlorine gas, corrosive sublimate being produced.

Corrosive sublimate, chloride of mercury, bichloride or *perchloride of mercury*, or *mercuric chloride*, is manufactured by heating 2 parts by weight of mercury with 3 parts of strong sulphuric acid, and evaporating to dryness, to obtain mercuric sulphate—

$$Hg + 2H_2SO_4 = HgSO_4 + 2H_2O + SO_2,$$

* It has been stated that by heating it for some time in a current of dry ammonia, it undergoes further change, becoming the oxide of mercurammonium, $(NHg''_2)_2O$, which is very explosive, and combines with water to form a hydrate which produces salts with the acids.

which is mixed with 1½ part of common salt and heated in glass vessels ($HgSO_4 + 2NaCl = Na_2SO_4 + HgCl_2$), when sodium sulphate is left, and the corrosive sublimate is converted into vapour, condensing on the cooler part of the vessel in lustrous colourless masses, which are very heavy (sp. gr. 5.4), and have a crystalline fracture. It fuses very easily (288° C.) to a perfectly colourless liquid, which boils at 303° C., emitting an extremely acrid vapour, which destroys the sense of smell for some time. This vapour condenses in fine needles, or sometimes in octahedra. Corrosive sublimate dissolves in twice its weight of boiling water, but requires 16 parts of cold water, so that the hot solution readily deposits long four-sided prismatic crystals of the salt. It is remarkable that alcohol and ether dissolve corrosive sublimate much more easily than water does, boiling alcohol dissolving about an equal weight of the chloride, and cold ether taking up one-third of its weight. By shaking the aqueous solution with ether, the greater part of the corrosive sublimate is removed, and remains dissolved in the ether which rises to the surface. An aqueous solution of ammonium chloride will take up corrosive sublimate more easily than pure water will, a soluble double chloride (*sal alembroth*) being formed, which may be obtained in tabular crystals, $HgCl_2.2NH_4Cl.H_2O$. A solution of corrosive sublimate in water containing sal-ammoniac is a very efficacious *bug-poison*.

Sulphuric acid does not decompose mercuric chloride, though it attacks mercurous chloride. Hydrochloric acid combines with it, forming crystalline compounds $HCl.HgCl_2$ and $HCl.2HgCl_2$, which lose HCl when exposed to air. A crystalline compound, $HgCl_2.H_2SO_4$, is formed by the action of hydrochloric acid on mercuric sulphate.

The poisonous properties of corrosive sublimate make it the most powerful antiseptic, and are very marked, so little as three grains having been known to cause death in the case of a child. The white of egg is commonly administered as an antidote, because it is known to form an insoluble compound with corrosive sublimate, so as to render the poison inert in the stomach. The compound of albumin with corrosive sublimate is also much less liable to putrefaction than albumin itself, and hence corrosive sublimate is sometimes employed for preserving anatomical preparations and for preventing the decay of wood (by combining with the vegetable albumin of the sap). Mercuric chloride unites with many other chlorides to form soluble double salts, and with mercuric oxide, forming several *oxychlorides*, which have no useful applications.

Mercuric chloride has been found native in one of the Molucca Islands.

White precipitate, employed for destroying vermin, is deposited when a solution of corrosive sublimate is poured into an excess of solution of ammonia; $HgCl_2 + 2NH_3 = NH_4Cl + NH_2Hg''Cl$ (*white precipitate*).

The true constitution of white precipitate has been the subject of much discussion, but the changes which it undergoes, under various circumstances, appear to lead to the conclusion that it represents ammonium chloride, NH_4Cl, in which half of the hydrogen has been displaced by mercury. When boiled with potash it yields ammonia and mercuric oxide; $NH_2Hg''Cl + KOH = NH_3 + HgO + KCl$. If it be boiled with water, it is only partly decomposed in a similar manner, leaving a yellow powder having the composition $(NH_2HgCl).HgO$, produced according to the equation $2(NH_2HgCl) + H_2O = NH_4Cl + (NH_2HgCl).HgO$. A compound corresponding with this yellow powder, but containing mercuric chloride in place of oxide, is precipitated when ammonia is gradually added to solution of corrosive sublimate

in large excess, the result being a compound of white precipitate with a molecule of undecomposed mercuric chloride ($NH_2HgCl).HgCl_2$. A compound having the same formula as the yellow powder, and probably identical with it, is obtained by the action of dilute hydrochloric acid on Millon's base (p. 499); it loses water at 200° C. and is *mercurammonium chloride hydrate*, $NHg_2Cl.H_2O$.

If white precipitate be heated to about 315° C., it evolves ammonia, and yields a sublimate of ammoniated mercuric chloride, $HgCl_2.NH_3$, leaving a red crystalline powder which is insoluble in water and in diluted acids, and is unchanged by boiling with potash; it may be represented as a compound of mercuric chloride with ammonia in which the whole of the hydrogen has been displaced by mercury, $N_2Hg''_3.2HgCl_2$. When strongly heated, white precipitate yields a sublimate of calomel: $3NH_2Hg''Cl = 3HgCl + N + 2NH_3$. White precipitate inflames in contact with chlorine or bromine. If it be mixed with about twice its weight of iodine and moistened with alcohol, an explosion occurs in about half an hour, from production of nitrogen iodide.

When solution of corrosive sublimate is added to a hot solution of sal-ammoniac, mixed with ammonia, a crystalline deposit is obtained on cooling the liquid; this is also obtained when ammoniacal mercuric chloride is precipitated by an alkaline carbonate; it is known as *fusible white precipitate*, and represents two molecules of ammonium chloride, in which one-fourth of the hydrogen has been displaced by mercury, its composition being $N_2H_6Hg''Cl_2$. The same compound is formed when white precipitate is boiled with solution of sal-ammoniac—

$$NH_2Hg''Cl + NH_4Cl = N_2H_6Hg''Cl_2.$$

The above compounds possess a special interest for the chemist, as they were among the first to attract attention to the mobility of the hydrogen in ammonia, which has since been so well exemplified in the artificial production of organic bases by the action of ammonia upon the iodides of the alcohol-radicles. The relation of these compounds to each other is here exhibited:

White precipitate	$NH_2Hg''Cl$
Produced with corrosive sublimate in excess .	$(NH_2HgCl).HgCl_2$
,, by boiling with water	$(NH_2HgCl).HgO$
,, ,, sal-ammoniac . .	$N_2H_6Hg''Cl_2$
,, by heating to 315° C.	$N_2Hg''_3.2HgCl_2$

According to Rammelsberg the infusible or true white precipitate loses half of its N as NH_3 when it is boiled with an alkali, while the fusible white precipitate loses three-quarters of its N as NH_3 under the same treatment; he concludes that they are both double compounds of ammonium chloride and mercurammonium chloride, the infusible being $NHg_2Cl.NH_4Cl$, and the fusible $NHg_2Cl.3NH_4Cl$.

294. *Calomel, subchloride* or *protochloride of mercury*, or *mercurous chloride* (HgCl), unlike corrosive sublimate, is insoluble in water, so that it is precipitated when hydrochloric acid or a soluble chloride is added to mercurous nitrate. The simplest mode of manufacturing it consists in intimately mixing a molecular weight of corrosive sublimate with an atomic weight of metallic mercury, a little water being added to prevent dust, drying the mixture thoroughly, and subliming it; $HgCl_2 + Hg = 2HgCl$. But it is more commonly made by adding another atomic weight of mercury to the materials employed in the preparation of corrosive sublimate; $HgSO_4 + Hg + 2NaCl = 2HgCl + Na_2SO_4$. The calomel condenses as a translucent, fibrous cake on the cool part of the subliming vessel. For medicinal purposes, the calomel is obtained in a very fine state of division by conducting the vapour into a large chamber so as to precipitate it in a fine powder by contact with a large volume of cold air. Steam is sometimes introduced to promote its fine division. Sublimed calomel always contains some corrosive sublimate, so that it must be thoroughly washed with water before being employed in medicine. When perfectly pure calomel is sublimed, a little is always decomposed during the process into metallic mercury and corrosive sublimate.

Calomel is met with either as a semi-transparent fibrous mass, or an

amorphous powder, with a slightly yellow tinge. Light slowly decomposes it, turning it grey from separation of mercury. It is heavier than corrosive sublimate (sp. gr. 7.18), and does not fuse before subliming; it may be obtained in four-sided prisms by slow sublimation. Dilute acids will not dissolve it, but boiling nitric acid gradually converts it into mercuric chloride and nitrate, which pass into solution. Boiling hydrochloric acid turns it grey, some mercury being separated, and mercuric chloride dissolved. Mercuric nitrate dissolves it, forming mercuric chloride and mercurous nitrate. Alkaline solutions convert it into black mercurous oxide, as is seen in *black-wash*, made by treating calomel with lime water; $Hg_2Cl_2 + Ca(OH)_2 = Hg_2O + CaCl_2 + H_2O$. Solution of ammonia converts it into a grey compound (NH_2Hg_2Cl), which is the analogue of white precipitate ($NH_2Hg''Cl$), containing Hg', in place of Hg''. Calomel is found as *horn quicksilver* at Idria and Almaden, crystallised in rhombic prisms.

It is asserted that calomel is dissociated by heat into Hg and $HgCl_2$ so that its vapour density does not decide its molecular weight. When, however, the vaporisation is performed in presence of $HgCl_2$, so that the dissociation is hindered (p. 313), the vapour density is found to be about 117.5, showing that HgCl is most probably the molecular formula for calomel. The presence of metallic mercury in calomel vapour is shown by the deposition of minute globules of mercury on a cold tube coated with gold immersed in the vapour at 440° C.

Mercurous iodide, HgI, is a green unstable substance, formed when iodine is triturated with an excess of mercury and a little alcohol, or by precipitating mercurous nitrate with potassium iodide. It owes its green colour to the presence of excess of mercury; when precipitated in a solution containing HNO_3 it is yellow. With care, it may be sublimed in yellow crystals, isomorphous with mercurous chloride, but if sharply heated it is decomposed into Hg and HgI_2. Potassium iodide decomposes it in a similar way, dissolving the mercuric iodide. When mercuric chloride is boiled with HCl and copper the solution gives with KI a dark red precipitate of *mercurous-mercuric iodide*, insoluble in excess of the KI.

Mercuric iodide, or *iodine scarlet*, HgI_2, is the bright red precipitate produced by potassium iodide in mercuric chloride. At the moment of precipitation it is yellow, rapidly becoming fawn coloured and red. When the dry mercuric iodide is heated, it becomes bright yellow at temperatures above 126° C., and remains so on cooling until touched with a hard body, when it becomes red again, the colour spreading from the point touched. Under the microscope, the red iodide is seen to be octahedral and the yellow to consist of rhombic tables. When the yellow iodide is heated, it fuses easily (238° C.), becomes brown, and is converted into a colourless vapour which condenses in yellow crystals on a cold surface.

A very beautiful experiment is made by gently heating mercuric iodide in a large porcelain crucible covered with a dial-glass; the yellow iodide is deposited in crystals projecting from the under surface of the glass, and if this be placed on the table with the crystals upwards, and some of these be touched with a needle, the red spots appear like poppies among corn, and the blush gradually spreads over the entire field, attended by a rustling movement caused by the change in crystalline form.*

The transformation of the yellow HgI_2 into the red HgI_2 evolves 3000 gram-units of heat. Mercuric iodide dissolves in hot alcohol, and crystallises in red octahedra. Ether also dissolves it. It is freely soluble in solutions of mercuric chloride and potassium iodide. The latter yields yellow prisms of $2(HgI_2.KI).3Aq$. The solution of this salt mixed with potash forms *Nessler's solution*, which gives a brown precipitate with very minute quantities of ammonia—

$$2HgI_2 + 3KOH + NH_3 = NHg_2I.H_2O + 3KI + 2H_2O.$$

The vapour density of mercuric iodide is of course very high, being 15.68 times that of air, showing that the formula HgI_2 represents two volumes.

295. **Sulphides of Mercury.**—When mercury is triturated with sulphur, the black *subsulphide of mercury*, or *mercurous sulphide* (Hg_2S), is

* The author is indebted for this experiment to Mr. Herbert Jackson, of King's College.

formed; it was termed by old writers *Ethiop's mineral*, and is an unstable compound easily resolved into metallic mercury and *mercuric sulphide* (HgS). The latter has been mentioned as the principal ore of mercury, and is important as composing *vermilion*. The native mercuric sulphide, or *cinnabar*, is found sometimes in amorphous masses, sometimes crystallised in six-sided prisms varying in colour from dark brown to bright red. It may be distinguished from most other minerals by its great weight (sp. gr. 8.2), and by its red colour when scraped with a knife. Neither hydrochloric nor nitric acid, separately, will dissolve it, but a mixture of the two dissolves it as mercuric chloride, with separation of sulphur. Some specimens of cinnabar have a bright red colour, so that they only require grinding and levigating to be used as vermilion; and if the brown cinnabar in powder be heated for some time at 120° F. (49° C.) with a solution of sulphur in potash, it is converted into vermilion.

Of the artificial mercuric sulphide there are two varieties—the black, which is precipitated when corrosive sublimate is added to hydrosulphuric acid or a soluble sulphide, and the red (vermilion), into which the black variety is converted by sublimation, or by prolonged contact with solutions of alkali sulphides containing excess of sulphur, though, so far as is known, the conversion is effected without chemical change, the red sulphide having the same composition as the black.

In Idria and Holland, 6 parts of mercury and 1 of sulphur are well agitated together in revolving casks for several hours, and the black sulphide thus obtained is sublimed in tall earthen pots closed with iron plates, when the vermilion is deposited in the upper part of the pots, and is afterwards ground and levigated. One of the wet processes for making vermilion consists in triturating 300 parts of mercury with 114 parts of sulphur for two or three hours and digesting the black product, at about 120° F. (49° C.), with 75 parts of caustic potash and 400 of water until it has acquired a fine red colour. The vermilion made by the dry process is the more highly prized. The permanence of vermilion paint, is, of course, attributable to the circumstance that it resists the action of light, of oxygen, carbonic acid, aqueous vapour, and even of the sulphuretted hydrogen, and sulphurous or sulphuric acid which contaminate the air of towns, whereas the red paints containing lead are blackened by sulphuretted hydrogen, and all vegetable and animal reds are liable to be bleached by atmospheric oxygen and by sulphurous acid.

The conversion of the black mercuric sulphide into the red form is quickly effected by boiling it with freshly prepared ammonium polysulphide (made by saturating ammonia with H_2S and dissolving sulphur in the liquid, gently warmed, until it has a dark sherry colour). If this solution be poured upon the freshly precipitated black sulphide, and boiled for a minute, the sulphide assumes a crystalline appearance, and a bright vermilion colour (Herbert Jackson). It appears that the black form is more soluble than the red, so that when the polysulphide solution becomes saturated with the black form it is supersaturated with the red, which therefore separates; another portion of the black then dissolves, and so on, until the conversion is complete.

If the black sulphide be boiled with potassium sulphide and potash, it is dissolved, and the solution deposits white needles of $HgS.K_2S.5H_2O$, which are decomposed by water.

When the black precipitated mercuric sulphide is boiled with solution of corrosive sublimate, it is converted into a white *chlorosulphide of mercury*, $HgCl_2.2HgS$, which is also formed when a small quantity of hydrosulphuric acid is added to corrosive sublimate, becoming yellow, brown, and black on adding more H_2S.

Vermilion may be prepared by adding $HgCl_2$ to a slight excess of dilute ammonia, nearly dissolving the precipitate in sodium thiosulphate (hyposulphite) and heating, when a bright yellow precipitate is obtained, which becomes bright red on boiling.

By suspending HgS in air-free water and passing H_2S, a dark-coloured solution of *colloidal mercuric sulphide* can be obtained.

At 1560° C. the vapour density of mercuric sulphide is 78, indicating that the molecule has dissociated into $Hg + Hg + S_2$.

Mercury belongs to the Magnesium family of metals (p. 383).

PLATINUM.

Pt = 193.3 parts by weight.

296. Platinum (*platina*, Spanish diminutive of silver) is remarkable for (1) its high specific gravity of 21.5; (2) its very high fusing-point, 1775° C.; (3) its slight expansion when heated, which allows it to be sealed into glass without cracking by unequal contraction on cooling; (4) its being unchanged by air at all temperatures; (5) its resistance to the action of strong acids; (6) its power of inducing the combination of oxygen with other bodies; (7) its being found in nature only in the metallic state. It is found distributed in flattened grains through alluvial deposits similar to those in which gold is found; indeed, these grains are generally accompanied by grains of gold, and of a group of very rare metals only found in platinum ores, viz., palladium, iridium, osmium, rhodium, and ruthenium. Russia furnishes the largest supply of platinum from the Ural Mountains, but smaller quantities are obtained from Brazil, Peru, Borneo, Australia, and California.

The process for obtaining the platinum in a marketable form is rather a chemical than a metallurgical operation. The ore containing the grains of platinum and the associated metals, is heated with hydrochloric acid to dissolve base metals, and then, in retorts, under slightly increased pressure to hasten the dissolution, with aqua regia, which dissolves palladium, rhodium, platinum, and a little iridium as chlorides. The osmium in the ore partly distils as osmic acid and partly remains undissolved as an alloy with the iridium (*osmiridium*), together with ruthenium, chrome iron ore, and titanic iron. The solution containing the platinum as $PtCl_4$ is neutralised with Na_2CO_3 and the palladium is precipitated as cyanide, $Pd(CN)_2$, by the addition of mercuric cyanide. The platinum is now precipitated by the addition of ammonium chloride, with which platinic chloride combines to form a yellow, sparingly soluble salt (ammonium platinochloride $(NH_4)_2PtCl_6$ or $2NH_4Cl.PtCl_4$).* This precipitate is collected, washed, and heated to redness, when all its constituents, except the platinum, are expelled in the form of gas, that metal being left in the peculiar porous condition in which it is known as *spongy platinum*. To convert this into compact platinum it is melted in a lime furnace by means of the oxyhydrogen blow-pipe (Fig. 243), whence it is poured into an ingot mould made of gas-carbon. The melted platinum absorbs oxygen, as melted silver does, and evolves it again on cooling.

This method is now modified by fusing the ore with 6 parts of lead, and treating the alloy with dilute nitric acid (1 : 8), which dissolves most of the lead, together

* When rhodium is present, the liquid from which this precipitate has been deposited will have a rose colour. The precipitate is then mixed with bisulphate of potassium and a little bisulphate of ammonium, and heated to redness in a platinum dish. The rhodium is then converted into a double sulphate of rhodium and potassium, which may be removed from the spongy platinum by boiling with water.

with copper, iron, palladium, and rhodium. The residue, containing platinum, lead, and iridium, is treated with dilute aqua regia, which leaves the iridium undissolved. The lead is precipitated by sulphuric acid, and the solution of platinic chloride treated as above.

Another process based upon the use of lead consists in fusing the platinum ore in a small reverberatory furnace, with an equal weight of lead sulphide and the same quantity of lead oxide when the sulphur and oxygen escape as SO_2, and the reduced lead dissolves the platinum, leaving undissolved a very heavy alloy of osmium and iridium, which sinks to the bottom. The upper part of the alloy of lead and platinum is then ladled out and cupelled (p. 465), when the latter metal is left in a spongy condition, the lead being removed in the form of oxide.

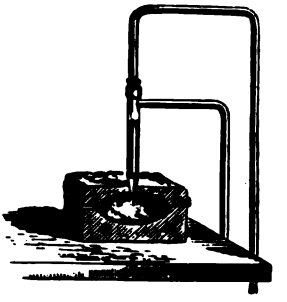


Fig. 243.

Its resistance to the action of high temperatures and of most chemical agents renders platinum of the greatest service in chemical operations. It will be remembered that platinum stills are employed, even on the large scale, for the concentration of sulphuric acid. In the form of basins, small crucibles, foil, and wire, this metal is indispensable to the analytical chemist. Unfortunately, it is softer than silver, and therefore ill-adapted for wear, and is so heavy that even small vessels must be made very thin in order not to be too heavy for a delicate balance. Commercial platinum generally contains a little iridium, which hardens it and increases its elasticity. Its malleability and ductility are very considerable, so that it is easily rolled into thin foil and drawn into fine wires; in ductility it is surpassed only by gold and silver, and it has been drawn, by an ingenious contrivance of Wollaston's, into wire of only $\frac{1}{30000}$th of an inch in diameter, a mile of which (notwithstanding the high specific gravity of the metal) would only weigh a single grain.

This remarkable extension of the metal was effected by casting a cylinder of silver around a very thin platinum wire obtained by the ordinary process of wire-drawing; when the cylinder of silver, with the platinum wire in its centre, was itself drawn out into an extremely thin wire, of course, the platinum core would have become inconceivably thin, and when the silver casing was dissolved off by nitric acid, this minute filament of platinum was left. Platinum is sometimes employed for the touch-holes of fowling-pieces on account of its resistance to corrosion. An alloy of 4 parts platinum, 3 parts silver, and 1 part copper is used for pens.

The widest application of platinum, however, is in the form of wire for conveying the electric current to the filament in an electric incandescence lamp. As such lamps must be vacuous the leading-in wires must be hermetically sealed in the glass, which is possible only with platinum, its coefficient of expansion being nearer to that of glass than is the coefficient of any other metal.

The remarkable power possessed by platinum, of inducing chemical combination between oxygen and other gases, has already been noticed. Even the compact metal possesses this property, as may be seen by heating a piece of platinum foil to redness in the flame of a gas-burner, rapidly extinguishing the gas, and turning it on again, when the cold stream of gas will still maintain the metal at a red heat, in consequence of the combination with atmospheric oxygen at the surface of the platinum.

A similar experiment may be made by suspending a coil of platinum wire in the

flame of a spirit lamp (Fig. 244), and suddenly extinguishing the flame, when the metal is intensely heated, by placing the mouth of a test-tube over it; the wire will continue to glow by inducing the combination of the spirit vapour with oxygen on its surface. By substituting a little ball of spongy platinum for the coil of platinum wire, and mixing some fragrant essential oil with the spirit, an elegant perfuming lamp has been contrived. Upon the same principle an instantaneous light apparatus has been made, in which a jet of hydrogen gas is kindled by impinging upon a fragment of cold spongy platinum, which at once ignites it by inducing its combination with the oxygen condensed within the pores of the metal (*Döbereiner's lamp*). Spongy platinum is obtained in a very active form by heating the ammonio-chloride of platinum very gently in a stream of coal gas or hydrogen as long as any fumes of HCl are evolved.

Fig. 244.

If platinum be precipitated in the metallic state from a solution, it is obtained in the form of a powder, called platinum black, which possesses this power of promoting combination with oxygen in the highest perfection. This form of platinum may be obtained by boiling solution of platinic chloride with Rochelle salt (potassium sodium tartrate), or by dropping it into a boiling mixture of 3 vols. glycerine and 2 vols. KOH of sp. gr. 1.08, when the platinum black is precipitated, and must be filtered off, washed, and dried at a gentle heat.

Platinum in this form is capable of absorbing 800 times its volume of oxygen, which does not enter into combination with it, but is simply condensed into its pores, and is available for combination with other bodies. A jet of hydrogen allowed to pass on to a grain or two of this powder is kindled at once, and if a few particles of it be thrown into a mixture of hydrogen and oxygen, explosion immediately follows. A drop of alcohol is also inflamed when allowed to fall upon a little of the powder. Platinum black loses its activity after having been heated to redness. It has been stated that platinum black is really an oxide, and that the combustion of hydrogen and oxygen in presence of platinum is to be explained by the formation, at first, of an unstable hydride of platinum, with development of heat, which is oxidised with a still further development of heat. By a continued repetition of these changes, the platinum is raised to the temperature necessary for ignition.

Although platinum resists the action of hydrochloric and nitric acids, unless they are mixed, and is unaffected at the ordinary temperature by other chemical agents, it is easily attacked at high temperatures by phosphorus, arsenic, carbon, boron, silicon, and by a large number of the metals; the caustic alkalies and alkaline earths also corrode it when heated, so that some discretion is necessary in the use of vessels made of this costly metal.* When platinum is alloyed with 10 parts of silver, both metals may be dissolved by nitric acid.

If platinum be dissolved in 4 or 5 parts of melted tin, and the alloy boiled with hydrochloric acid mixed with an equal bulk of water, glistening scales are left, resembling graphite, and soiling the fingers. This contains platinum, tin, chlorine, hydrogen, and oxygen. By treatment with warm dilute ammonia, it becomes brownish, and when dried in a vacuum over sulphuric acid, has the composition $Pt_2Sn_3O_4H_2$. When this is heated in dry oxygen, it becomes $Pt_2Sn_3O_4$. Heated in hydrogen it leaves a greyish almost infusible powder containing Pt_2Sn_3.

297. OXIDES OF PLATINUM.—Only one compound of platinum with oxygen is known in the separate state, the other having been obtained in combination with water. *Platinous oxide*, PtO, is precipitated as a black hydrate by decomposing platinous chloride with potash, and neutralising the solution with dilute sulphuric acid. It is a feeble base, and decomposes when heated, leaving metallic platinum. *Platinic oxide*, PtO_2, is also a weak base, but is characteristically an acid oxide.

Platinic hydroxide, $Pt(OH)_4$, is obtained by boiling platinic chloride with potash, and treating the precipitate with acetic acid; this leaves a nearly white powder, $Pt(OH)_4.2H_2O$. At 100° C. this becomes brown $Pt(OH)_4$. Acids dissolve it, forming

* When platinum leaf is heated with HCl at 150° in a sealed tube it dissolves, but the chloride is subsequently reduced by the hydrogen evolved, and the metal reappears as crystals on the sides of the tube. The same has been observed of gold and silver leaf.

platinic salts. Alkalies dissolve it, forming platinates. Heat reduces the oxides and hydroxides to metallic platinum.

Sodium platinate, $Na_2O.3PtO_2.6Aq$, may be crystallised from a solution of the hydroxide in soda. *Calcium platinate* is convenient for the separation of platinum from iridium, which is generally contained in the commercial metal; for this purpose, the platinum is dissolved in nitro-hydrochloric acid, the solution evaporated till it solidifies on cooling, the mixed chlorides of iridium and platinum dissolved in water, and decomposed with an excess of lime *without exposure to light*; the platinum then passes into solution as calcium platinate, and the platinic acid may be separated as a calcium salt from the filtered solution, by exposure to light. If platinic hydroxide be dissolved in diluted sulphuric acid and the solution mixed with excess of ammonia, a black precipitate of *fulminating platinum* is obtained, which detonates violently at about 400° F. (204° C.). This compound is said to have a composition corresponding with the formula $N_2H_2Pt^{IV}.4H_2O$, or a combination of water with a double molecule of ammonia (N_2H_6), in which 4 atoms of hydrogen are exchanged for 1 atom of tetravalent platinum.

298. **Chlorides of Platinum.**—The *perchloride* or *platinic chloride*, ($PtCl_4$), is the most useful salt of the metal, and may be prepared by dissolving scraps of platinum-foil in a mixture of four measures of hydrochloric acid with one of nitric acid (6.5 grams of platinum require 56 c.c. of hydrochloric acid), evaporating the liquid at a gentle heat to the consistence of a syrup, redissolving in hydrochloric acid, and again evaporating to expel excess of nitric acid. The syrupy liquid solidifies, on cooling, to a red-brown mass, which is very deliquescent, and dissolves easily in water or alcohol to a red-brown solution. If the concentrated solution be allowed to cool before all the free hydrochloric acid has been expelled, long brown prismatic crystals of a combination of platinic chloride with hydrochloric acid are obtained ($PtCl_4.2HCl.6Aq$). If these are heated in dry HCl, the anhydrous $PtCl_4$ is obtained in a non-deliquescent condition; it decomposes Na_2CO_3, evolving CO_2. Platinic chloride is remarkable for its disposition to form sparingly soluble double chlorides with the chlorides of the alkali metals and the hydrochlorides of organic bases, a property of great value to the chemist in effecting the detection and separation of these bodies. These double chlorides are generally regarded as *platinochlorides* or *chloroplatinates*, derived from *hydrogen platinochloride*, or *chloroplatinic acid*, H_2PtCl_6.

A good example of this has lately been afforded in the separation of potassium, rubidium, and cæsium. The chlorides of these three metals having been separated from the various other salts contained in the mineral water in which they occur, are precipitated with platinic chloride, which forms combinations with all the three chlorides. The platino-chloride of potassium is more easily dissolved by boiling water than are those of rubidium and cæsium, and is removed by boiling the mixed precipitate with small portions of water as long as the latter acquires a yellow colour. The remaining platino-chlorides of rubidium and cæsium are then heated in a current of hydrogen, which reduces the platinum to the metallic state, and the chlorides may then be extracted by water, in which they are very soluble.

Potassium platinochloride ($2KCl.PtCl_4$) forms minute yellow octahedral crystals; those of rubidium and cæsium have a similar composition and crystalline form. *Sodium platinochloride* differs from these in being very soluble in water and alcohol; it may be crystallised in long red prisms, having the composition $2NaCl.PtCl_4.6Aq$. *Ammonium platinochloride* ($2NH_4Cl.PtCl_4$) has been already noticed as the form in which platinum is precipitated in order to separate it from other metals. It crystallises, like the potassium-salt, in yellow octahedra, which are very sparingly soluble in water and insoluble in alcohol. It is the form

into which nitrogen is finally converted in analysis in order to determine its weight. When heated to redness, this salt leaves a residue of spongy platinum. Silver nitrate, added in excess to platinic chloride containing HCl, precipitates all the platinum as $2AgCl.PtCl_4$, a yellow precipitate decomposed by water.

Platinic chloride is sometimes used for browning gun-barrels, &c., under the name of *muriate of platina*.

Protochloride, or *platinous chloride* ($PtCl_2$).—Platinic chloride may be heated to 450° F. (232° C.) without decomposition, but above that temperature it evolves chlorine, and is slowly converted into the platinous chloride, which is reduced, at a much higher temperature, to the metallic state. Platinous chloride forms a dingy green powder, which is insoluble in water and in HNO_3 and H_2SO_4, but dissolves in hot HCl, and in solution of platinic chloride, yielding in the former a bright red, in the latter a very dark brown-red solution. Platinous chloride is capable of absorbing ethylene, C_2H_4. At 250° C. it absorbs CO and forms the crystalline compounds $PtCl_2.CO$, $PtCl_2(CO)_2$, and $(PtCl_2)_3(CO)_3$, and the non-volatile compound $PtCl_2.2COCl_2$; the first of these volatilises unchanged. The solution of $PtCl_2$ in HCl is not precipitated by KCl, but a soluble double chloride ($2KCl.PtCl_2$) may be crystallised from the liquid. If NH_4Cl be added to the hydrochloric solution, a double salt, $2NH_4Cl.PtCl_2$, *ammonium chloroplatinite*, may be obtained in yellow crystals by evaporation. If, instead of NH_4Cl, free NH_3 be added in excess to the boiling solution of platinous chloride in HCl, brilliant green needles (*green salt of Magnus*) are deposited on cooling, which contain the elements of platinous chloride and ammonia, $PtCl_2(NH_3)_2$; but from the behaviour of this compound with chemical agents, its true formula would appear to be $N_2H_6Pt''Cl_2$, in which the place of two atoms of hydrogen in 2 molecules of NH_4Cl is occupied by platinum. By heating this salt with an excess of ammonia, the solution, on cooling, deposits yellowish-white prismatic crystals of *diplatosamine hydrochloride*, $N_4H_{10}Pt''.2HCl.Aq$, the production of which may be represented by the equation $N_2H_6Pt''Cl_2 + 2NH_3 = N_4H_{10}Pt''.2HCl$. By decomposing a solution of this salt with silver sulphate, the *diplatosamine sulphate* is obtained.

$$N_4H_{10}Pt''.2HCl + Ag_2SO_4 = N_4H_{10}Pt''.H_2SO_4 + 2AgCl.$$

When the solution of diplatosamine sulphate is treated with barium hydroxide, barium sulphate is precipitated, and a powerfully alkaline solution is obtained, which yields crystals of *diplatosamine hydrate*, $N_4H_{10}Pt''.2H_2O$, a strong alkali which may be regarded as a compound of water with 4 molecules of ammonia (N_4H_{12}), in which two atoms of hydrogen are exchanged for platinum. The diplatosamine hydrate has a strong resemblance to the alkalies, eagerly absorbing CO_2 from the air, and expelling NH_3 from its salts. When the hydrate of diplatosamine is heated to 110° C. it gives off water and ammonia, and becomes converted into a grey insoluble substance, which is *platosamine hydrate*, $N_2H_4Pt''.H_2O$, and may be regarded as a compound of water with a double molecule of ammonia (N_2H_6), in which one-third of the hydrogen is exchanged for platinum. This substance is also a base, and forms salts, most of which are insoluble; the *hydrochloride* ($N_2H_4Pt.2HCl$) is isomeric with the green salt of Magnus, and may be obtained from that compound by dissolving in a hot solution of $(NH_4)_2SO_4$ from which it crystallises on cooling.*

If the *platosamine hydrochloride*, suspended in boiling water, be treated with chlorine, it is converted into *platinamine hydrochloride*, $N_2H_2Pt^{iv}.4HCl$. The conversion of the platosamine hydrochloride into platinamine hydrochloride may be represented by the equation $N_2H_4Pt.2HCl + Cl_2 = N_2H_2Pt.4HCl$. By boiling the platinamine hydrochloride with silver nitrate, it is converted into *platinamine nitrate*, $N_2H_2Pt(HNO_3)_4$; and when this is dissolved in boiling water and decomposed by ammonia, the *platinamine hydrate* ($N_2H_2Pt.4H_2O$) is obtained in yellow prismatic crystals, having the same composition as that assigned to fulminating platinum.

* The salts of diplatosamine are distinguished from those of platosamine by the action of nitrous acid, which gives a fine blue or green precipitate or coloration with the former. For the cause of this change, and for many other interesting points in the history of these platinum compounds, the reader is referred to the elaborate and accurate memoir by Hadow, *Journal of the Chemical Society*, August 1866.

Some of the salts of *diplatinamine* ($N_4H_8Pt^{IV}$) have been obtained, this base being derived from 4 molecules of ammonia in which H_4 have been exchanged for Pt^{IV}.

Potassium platinonitrite, $K_2Pt(NO_2)_4$, crystallises when a hot mixture of potassium nitrite and potassium platinous chloride solution is allowed to cool; it readily combines with 2 atomic proportions of a halogen. The acid $H_2Pt(NO_2)_4$ has been prepared.

Platinic iodide, PtI_4, is a dark brown amorphous substance which is soluble in HI, yielding a purple-red solution containing $2HI.PtI_4.9Aq$, which may be crystallised. Hence the dark red colour when an acid solution of $PtCl_4$ is added to potassium iodide.

The *sulphides of platinum* correspond in composition with the oxides and chlorides, and may be obtained by the action of hydrosulphuric acid upon the respective chlorides, as black precipitates. PtS_2 combines with alkaline sulphides to form soluble compounds. $K_2S.3PtS.PtS_2$ is obtained by fusing spongy platinum with KOH and sulphur.

Platinum phosphide, PtP_2, and *arsenide*, $PtAs_2$, are lustrous metallic bodies formed by direct combination at a high temperature.

PALLADIUM, Pd = 105.2.

299. This metal is found in small quantity associated with native gold and platinum. It presents a great general resemblance to platinum, but is distinguished therefrom by being far more easily oxidised, and by forming an insoluble cyanide. This circumstance is taken advantage of in separating palladium from the platinum ores (p. 504). The cyanide yields spongy palladium when heated, which may be fused in the same manner as platinum. When alloyed with native gold, palladium is separated by fusing the alloy with silver, and boiling it with nitric acid, which leaves the gold undissolved. The silver is precipitated from the solution as chloride, by adding NaCl, and metallic zinc is placed in the liquid, which precipitates the palladium, lead, and copper as a black powder. This is dissolved in HNO_3, and the solution mixed with an excess of NH_3, which precipitates the lead oxide, leaving the copper and palladium in solution. On adding HCl in slight excess, a yellow precipitate of *palladamine hydrochloride* ($N_2H_4Pd.2HCl$) is obtained, which leaves metallic palladium when heated.

Palladium is much lighter (sp. gr. 11.8) than platinum; it is malleable and ductile like that metal from which it is distinguished by being stained black by an alcoholic solution of iodine. It is capable of being highly polished and is useful for mirrors. It melts at 1500° C. It is unchangeable in air unless heated, when it becomes blue from superficial oxidation, but regains its whiteness when further heated, the oxide being decomposed. Unlike platinum, it may be dissolved by nitric acid, forming *palladium nitrate*, $Pd(NO_3)_2$, which is sometimes employed in analysis for precipitating iodine from the iodides, in the form of black *palladium iodide* (PdI_2). Palladium is useful, on account of its hardness, lightness, and resistance to tarnish, in the construction of philosophical instruments; alloyed with twice its weights of silver, it is used for small weights. Its capacity for absorbing hydrogen has been already noticed (p. 49).

Palladium forms three *oxides*; Pd_2O is formed when the metal is heated in air; PdO is left when $Pd(NO_3)_2$ is gently heated; PdO_2 is precipitated by boiling $PdCl_4$ with Na_2CO_3. *Palladic chloride* ($PdCl_4$) is very unstable, being easily decomposed, even in solution, into *palladous chloride* ($PdCl_2$) and free chlorine. The latter chloride is reduced by hydrogen in the cold, and may be applied as a test for this gas. Both the chlorides form double salts with the alkali chlorides; *ammonium chloropalladite*, $PdCl_2.2NH_4Cl$, has a dark green colour. PdCl is said to be formed when $PdCl_2$ is gently heated. Pulverulent *palladium carbide* is formed when the metal is heated in the flame of a spirit-lamp, or in gaseous hydrocarbons.

RHODIUM, Rh = 102.2.

300. Rhodium, another of the metals associated with the ores of platinum, has acquired its name from the red colour of many of its salts (*ῥόδον, a rose*). It is obtained from the solution of the ore in *aqua regia* by precipitating the platinum with ammonium chloride, neutralising with sodium carbonate, adding mercuric cyanide to separate the palladium, and evaporating the filtered solution to dryness with excess of hydrochloric acid. On treating the residue with alcohol, the double chloride of rhodium and sodium is left undissolved as a red powder. By

heating this in a tube through which hydrogen is passed, the rhodium is reduced to the metallic state, and the sodium chloride may be washed out with water, leaving a grey powder of metallic rhodium, which is fused by the oxyhydrogen blow-pipe at 200° C., and forms a very hard malleable metal (sp. gr. 12.1) not dissolved even by *aqua regia*, although this acid dissolves it in ores of platinum, because it is alloyed with other metals. If platinum be alloyed with 30 per cent. of rhodium, however, it is not affected by *aqua regia*, which will probably render the alloy useful for chemical vessels. Rhodium may be brought into solution by fusing it with bisulphate of potash, when SO_2 escapes, and a double sulphate of rhodium and potassium is formed, which gives a pink solution in water. When rhodium is melted with zinc and the alloy is boiled with an acid, the rhodium is left as a black powder which is apparently an allotropic form of the metal, for when it is heated it explodes, but remains metallic rhodium. Finely divided rhodium is oxidised, when heated in air, to RhO. There appear to be three other *oxides*, namely, Rh_2O_3, which is left when the nitrate is gently heated; RhO_2, formed when the metal is fused with KOH and KNO_3; RhO_3, formed by heating the hydrated dioxide (which is a green precipitate obtained when chlorine is passed into potash containing Rh_2O_3) with nitric acid. The sesquioxide (Rh_2O_3) is the most stable of these; it is not easily decomposed by heat, and is insoluble in acids, though it is a basic oxide, and its salts, which have a red colour, are obtained by indirect methods.

The salts of rhodium are only of one type—RX_3. *Rhodium trichloride*, $RhCl_3$, obtained by heating the metal in chlorine, has a brownish-red colour and is insoluble; it may, however, be obtained in a red solution by dissolving the hydrated Rh_2O_3 in HCl. Rhodium recalls chromium in that its salts are capable of existing in two forms: thus, when the red solution of rhodium chloride is boiled with a strong solution of alkali, black $Rh(OH)_3$ is thrown down, but when the alkali is added by degrees, yellow $Rh(OH)_3$ is precipitated: this dissolves to a yellow solution in acids, which becomes red only on boiling. Like chromium, too, rhodium salts form a series of amines (p. 434). $RhCl_3$ forms two classes of double salts with the alkali chlorides—for instance, $K_3RhCl_6.3H_2O$ and $K_2RhCl_5.H_2O$. The double chloride of rhodium and sodium ($3NaCl.RhCl_3$) is prepared by heating a mixture of pulverulent rhodium and NaCl in a current of chlorine. It crystallises in red octahedra with 9Aq. On boiling a solution of $RhCl_3$ with NH_3 in excess, a yellow ammoniated salt ($RhCl_3.5NH_3$) may be crystallised, from which the metallic rhodium may be obtained by ignition.

With sulphur, rhodium combines energetically at a high temperature; a monosulphide and a sesquisulphide have been obtained.

An alloy of gold with between 30 and 40 per cent. of rhodium has been found in Mexico.

An alloy of platinum with 10 per cent. of rhodium is used as one of the metals, platinum being the other, of the thermo-electric couple used as a pyrometer.

OSMIUM, Os = 189.6.

301. This metal is characterised by its yielding a very volatile acid oxide (*perosmic anhydride*, OsO_4), the vapours of which have a very irritating odour (ὀσμή, *odour*). It occurs in the ores of platinum in flat scales, consisting of an alloy of osmium, iridium, ruthenium, and rhodium. This alloy is also found associated with native gold, and, being very heavy, it accumulates at the bottom of the crucible in which the gold is melted. The osmium alloy is extremely hard, and has been used to tip the points of gold pens. When a grain of it happens to be present in the gold which is being coined, it often seriously injures the die. When the platinum ore is treated with *aqua regia*, this alloy is left undissolved, together with grains of chrome-iron ore and titanic iron. To extract osmium from this residue, it is heated in a porcelain tube through which a current of dry air is passed, when the osmium is converted into perosmic anhydride, the vapour of which is carried forward by the current of air and condensed in bottles provided to receive it. The *perosmic anhydride* forms colourless prismatic crystals which fuse and volatilise below the boiling-point of water, yielding a most irritating vapour, resembling chlorine. It is very soluble in water, giving a solution which exhales the same odour and stains the skin black; tincture of galls gives a blue precipitate with the solution. Its acid properties are feeble, for it neither reddens litmus nor decomposes the carbonates, and its salts are decomposed by boiling their solutions. Its solution in HCl gives a black precipitate of OsS_4 with H_2S. By

passing a mixture of CO and vapour of OsO_4 through a red-hot porcelain tube, amorphous osmium is obtained, and may be converted into the crystalline form by fusing it with tin and dissolving in HCl, when blue lustrous cubical crystals of osmium are obtained, which scratch glass, and are heavier than any other body, having the specific gravity 22.48. It can be fused in the electric arc.

By dissolving perosmic anhydride in potash, *potassium perosmate*, $KOsO_4$, is supposed to be formed, but this has not been isolated. When alcohol is added to this solution the OsO_4, is presumably reduced to OsO_3, for rose-coloured crystals of *potassium osmate*, $K_2O.OsO_3.2H_2O$, are deposited; by treating this salt with nitric acid, *osmic acid*, H_2OsO_4, is obtained as a sooty-black powder, which tends to oxidise in air, yielding an odour of perosmic anhydride.

When OsO_4 is dissolved in solution of SO_2, *osmium sulphite*, $OsSO_3$, is obtained; this is almost the only osmium oxy-salt which is known. By adding an alkali to the solution, hydrated osmium *monoxide*, $OsO.nH_2O$, is obtained as a blue-back powder soluble in HCl to a blue solution and easily oxidised. Os_2O_3 and OsO_2 are obtained by heating potassium *osmochloride*, $3KCl.OsCl_3$, and *osmichloride*, $2KCl.OsCl_4$, respectively with an alkali carbonate in absence of air.

Osmium dichloride, $OsCl_2$, and *tetrachloride*, $OsCl_4$, are obtained as two distinct sublimates when the metal is heated in chlorine; $OsCl_2$ is less votatile, and forms green needles, whilst $OsCl_4$ is a dark-red powder. By mixing Os with KCl, heating the mixture in chlorine, treating the mass with water, and evaporating, red octahedra of $2KCl.OsCl_4$ separate, whilst from the mother liquor $3KCl.OsCl_3.3H_2O$ is crystallised. When osmic acid is heated with HCl and alcohol and the solution is evaporated, crystals having the formula $Os_2Cl_7.7H_2O$ are formed; these are red when dry, but dissolve in water and in alcohol to a green solution; by adding KCl to the alcoholic solution, K_2OsCl_6 is precipitated, and when the filtrate is evaporated, $OsCl_3.3H_2O$ crystallises.

Several compounds of osmium salts with ammonia (*osmamines*) are known, and a "*potassium osmiamate*," $KNOsO_3$, is obtained by the action of NH_3 on a solution of OsO_4 in KOH.

RUTHENIUM, Ru = 100.9.*

302. In the process of extracting osmium from the residue left on treating the platinum ore with *aqua regia*, by heating in a current of air, square prismatic crystals of *ruthenium dioxide* (RuO_2) are deposited nearer to the heated portion of the tube than the perosmic anhydride, for the dioxide is not itself volatile, being only carried forward mechanically; or it may be that the volatile RuO_4 is formed in the hot part of the tube, and dissociated into RuO_2 and O_2 in a cooler part. When RuO_2 is heated in H the metal is obtained; it can be melted (1800° C.) in the electric arc, and is then a grey metal, very hard, brittle when cold but malleable when hot; its sp. gr. is 12.26. It is insoluble in acids. When fused with zinc it yields an allotropic form similar to that described above for rhodium.

When ruthenium is heated at 1000° C. in oxygen the volatile oxide RuO_4 is formed, and may be isolated if rapidly cooled, but when allowed to cool slowly it decomposes. The same oxide may be obtained by heating ruthenium with KNO_3 and KOH, and saturating the solution of the fused mass with chlorine, when RuO_4 sublimes. It is soluble in water, melts at 25.5°, and sublimes easily; at 107° it decomposes explosively. It is decomposed by light, yielding, apparently, RuO_3.

The oxides RuO and Ru_2O_3 are probably also known. *Ruthenates* analogous to the osmates have been prepared. $RuCl_2$ and $RuCl_3$ are formed when the metal is heated in chlorine. The latter is insoluble in cold water, but dissolves in absolute alcohol to a purple-violet solution which becomes indigo-blue from absorption of water and formation of $RuCl_2.OH$; the solution gradually deposits $Ru(OH)_3$. Double chlorides analogous to those of osmium exist.

Sulphates corresponding with RuO and Ru_2O_3 have been obtained.

IRIDIUM, Ir = 191.5.

303. Named from Iris, *the rainbow*, in allusion to the varied colours of its compounds, this metal occurs in the insoluble alloy from the platinum ores. It is also sometimes found separately, and occasionally alloyed with platinum, the alloy

* A mineral found in Borneo, and named *laurite*, contains sulphides of ruthenium and osmium. It forms small lustrous granules.

crystallising in octahedra, which are even heavier than platinum (sp. gr. 22.3). If the insoluble osmiridium alloy left by *aqua regia* be mixed with common salt and heated in a current of chlorine a mixture of the sodio-chlorides of the metals is obtained and may be extracted by boiling water. If the solution be evaporated and distilled with nitric acid, the osmium is distilled off as perosmic anhydride, and by adding ammonium chloride to the residual solution, the iridium is precipitated as a dark red-brown ammonio-chloride, $2NH_4Cl.IrCl_4$, which leaves metallic iridium when heated. Like platinum, it then forms a grey spongy mass, but is oxidised when heated in air, and may be fused (2200° C.) with the oxy-hydrogen blowpipe to a hard brittle mass (sp. gr. 22.4), which does not oxidise in air. Like rhodium, it is not attacked by *aqua regia*, unless alloyed with platinum. By fusion with zinc it yields an allotropic form similar to that described for rhodium. The product of the oxidation of finely divided iridium in air is the *sesquioxide* (Ir_2O_3), which is a black powder used for imparting an intense black to porcelain; it is insoluble in acids. The *monoxide* (IrO) is also more easily acted upon by alkalies than by acids; its solution in potash becomes blue when exposed to air, from the formation of the *dioxide* (IrO_2). The *trioxide* (IrO_3) is green. The *dichloride* ($IrCl_2$) and *tetrachloride* ($IrCl_4$) of iridium resemble the corresponding chlorides of platinum in forming double salts with the alkali chlorides. There is also a *trichloride* ($IrCl_3$), the solution of which has a green colour, and gives a yellow precipitate with mercurous nitrate, and a blue precipitate, soon becoming white, with silver nitrate. Double compounds of the chloride with ammonia (*iridamines*) are known. Iridium resembles palladium in its disposition to combine with carbon when heated in the flame of a spirit-lamp.

Salts of iridium correspond with the oxides IrO and Ir_2O_3.

An *iridio-platinum alloy* containing from 15 to 20 per cent. of iridium has been found very useful for making standard rules and weights, on account of its indestructibility, extreme rigidity, hardness, and high density.

The following table exhibits a general view of the analytical process by which the remarkable metals associated in the ores of platinum may be separated from each other, omitting the minor details which are requisite to ensure the purity of each metal:

Analysis of the Ore of Platinum.

Boil with *aqua regia*.

<table>
<tr><td colspan="3">Dissolved;
PLATINUM, PALLADIUM, RHODIUM.
Add ammonium chloride.</td><td colspan="3">Undissolved;
IRIDIUM, OSMIUM, RUTHENIUM.
Chrome iron, Titanic iron, &c.
Heat in a current of dry air.</td></tr>
<tr><td rowspan="2">Precipitated;
PLATINUM
as
$2NH_4Cl.PtCl_4$.</td><td colspan="2">Solution;
Neutralise with sodium carbonate;
add mercuric cyanide.</td><td rowspan="2">Volatilised;
OSMIUM
as OsO_4.</td><td rowspan="2">Carried forward by the current;
RUTHENIUM
as RuO_2.</td><td colspan="2">Residue;
Mix with sodium chloride, and heat in a current of chlorine.
Treat with boiling water.</td></tr>
<tr><td>Precipitated;
PALLADIUM
as $PdCy_2$.</td><td>Solution;
Evaporate with hydrochloric acid.
Treat with alcohol.
Insoluble;
RHODIUM
as $3NaCl.RhCl_3$.</td><td>Dissolved;
IRIDIUM
as
$2NaCl.IrCl_4$.</td><td>Residue;
Titanic iron,
Chrome iron,
&c.</td></tr>
</table>

304. The *platinoid metals* fall into two classes according to the proximity which exists between their specific gravities and between their atomic weights—viz., Os, Ir, Pt, and Ru, Rh and Pd. Gold is associated with the former class by its sp. gr., atomic weight, and insolubility, whilst silver is related to the latter class also by its atomic weight and sp. gr., and by its solubility in nitric acid, resembling that of Pd. The first member of each class (Os and Ru) gives a volatile tetroxide, whilst the highest state of oxidation of the remaining metals is RO_3. In the periodic classification (p. 302), they fall in the same group as Fe, Co and Ni, with which they have several features in common, such as the marked colour of their salts, their infusibility and their tendency to form salts in two stages of oxidation.

GOLD.

Au = 195.7 parts by weight.

305. The individuality of gold among metals is strongly marked, on account of its colour, its high specific gravity, 19.3, its extreme malleability and ductility, its perfect resistance to air, its high conducting power for heat and electricity, its high fusing-point, 1064° C., its resistance to acids, and its rarity and consequent intrinsic value. Gold is one of those few metals which are always found in the metallic state, and is remarkable for the extent to which it is distributed, though in small quantities, over the surface of the earth. The principal supplies of this metal are derived from Australia. the Transvaal Colony, California, Mexico, Brazil, Peru, and the Ural Mountains. Small quantities have been occasionally met with in our own islands, particularly at Wicklow, at Cader Idris in Wales, Leadhills in Scotland, and in Cornwall.

The mode of the occurrence of gold in the mineral kingdom resembles that of the ore of tin, for it is either found disseminated in the primitive rocks, or in alluvial deposits of sand, which appear to have been formed by the disintegration of those rocks under the continued action of torrents. In the former case, the gold is often found crystallised in cubes and octahedra, or in forms derived from these, and sometimes aggregated together in dendritic or branch-like forms. In the alluvial deposits, the gold is usually found in small scales (gold dust), but sometimes in masses of considerable size (nuggets), the rounded appearance of which indicates that they have been subjected to attrition. Australian gold is the purest, especially that from Victoria.

The extraction of the particles of gold from the alluvial sands is effected by taking advantage of the high specific gravity of the metal (19.3), which causes it to remain behind, whilst the sand, which is very much lighter (sp. gr. 2.6), is carried away by water. The washing is commonly performed by hand, in wooden or metal bowls, in which the sand is shaken up with water, and the lighter portions dexterously poured off, so as to leave the grains of gold at the bottom of the vessel. On a somewhat larger scale, the auriferous sand is washed in a *cradle* or inclined wooden trough, furnished with rockers, and with an opening at the lower end for the escape of the water. The sand is thrown on to a grating at the head of the cradle, which retains the large pebbles, whilst the sand and gold pass through, the former being washed away by a stream of water which is kept flowing through the trough.

When the gold is disseminated through masses of quartz or other rock, much labour is expended in crushing the latter before the gold can be separated. This is effected either by passing the coarse fragments between heavy rollers of hard cast-iron, or by stamping them, with wooden beams shod with iron, in troughs through which water is continually flowing.

In some cases it is found advantageous to smelt the ore by fusing it with some substance capable of uniting with the gold, and of being afterwards readily separated from it. Lead is peculiarly adapted for this purpose; the crushed ore is mixed with a suitable proportion, either of metallic lead, or of litharge (oxide of lead) and charcoal, or even

of galena (sulphide of lead), together with some lime and oxide of iron or clay, to flux the silica, and is fused on the hearth of a reverberatory furnace, when the fused lead dissolves the particles of gold, and collects beneath the lighter slag. The lead is afterwards separated from the gold by cupellation (see p. 464).

In smelting the ores of gold in Hungary, the metal is concentrated by means of sulphide of iron. The ore consists of quartz and iron pyrites (FeS_2), containing a little gold. On fusing the crushed ore with lime, to flux the quartz, the pyrites loses half its sulphur, and becomes ferrous sulphide (FeS), which fuses and sinks below the slag, carrying with it the whole of the gold. If this product be roasted so as to convert the iron into oxide, and be then again fused with a fresh portion of the ore, the oxide of iron will flux the quartz, whilst the fresh portion of FeS will carry down the whole of the gold contained in both quantities of ore. This operation having been repeated until the FeS is rich in gold, it is fused with a certain quantity of lead, which extracts the gold and falls to the bottom. The lead is then cupelled in order to obtain the gold.

When the ores of lead, silver, or copper contain gold, it is always found to have accompanied the silver extracted from them, and is separated from it by a process to be presently noticed.

Gold is sometimes separated from the impurities remaining with it after extraction by washing, by the process of amalgamation, which consists in shaking the mixture with mercury in order to dissolve the gold-dust, and straining the liquid amalgam through chamois leather, which allows the excess of mercury to pass through, but retains the solid portion containing the gold, from which the mercury is then separated by distillation.*

Chlorine (or bromine) water is sometimes employed to extract the gold by converting it into $AuCl_3$, the gold being afterwards precipitated from the solution by adding ferrous sulphate, or by filtration through charcoal which retains the gold, which is subsequently separated by burning the charcoal.

The *cyanide process*, particularly applicable to the extraction of gold from the *tailings* or material which contains the metal so finely divided that it has escaped separation by the washing process, depends on the solubility of gold in a 1 per cent. solution of potassium cyanide in presence of air; $Au_2 + 4KCN + H_2O + O = 2(AuCN.KCN) + 2KOH$.† The soluble double cyanide of Au and K is decomposed either by running the solution through boxes containing zinc which precipitates the gold, or by electrolysing the solution when the gold is deposited on the cathode.

Gold, as found in nature, is generally alloyed with variable proportions of silver and copper, the separation of which is the object of the gold refiner. It may be effected by means of nitric acid, which will dissolve the silver and copper, provided that they do not bear too small a proportion to the gold. Sulphuric acid, however, being very much cheaper, is generally employed. The alloy is fused and poured into water, so as to granulate it and expose a larger surface to the action of the acid; it is then boiled with concentrated sulphuric acid (oil of vitriol), which converts the silver and the copper into sulphates, with

* A small quantity of sodium dissolved in the mercury has been found very materially to facilitate the amalgamation of gold and silver ores, apparently because the amalgam of sodium is more highly electro-positive than mercury, in relation to the gold.

† It is said that H_2O_2 is produced, the equation being—

$$Au_2 + 8KCN + O_4 + 4H_2O = 2KAu(CN)_4 + 6KOH + H_2O_2.$$

evolution of sulphurous acid gas, whilst the gold is left untouched. In order to recover the silver from the solution of the sulphates in water, scraps of copper are introduced into it, when that metal decomposes the sulphate of silver, producing sulphate of copper, and causing the deposition of the silver in the metallic state. Finally, the sulphate of copper may be obtained from the solution by evaporation and crystallisation. This process is so effectual when the proportion of gold in an alloy is very small, that even $\frac{1}{20}$ part of this metal may be profitably extracted from 100 parts of an alloy, and much gold has been obtained in this way from old silver plate, coins, &c., which were manufactured before so perfect a process for the separation of these metals was known. On boiling old silver coins or ornaments with nitric acid, they are generally found to yield a minute proportion of gold in the form of a purple powder. But this plan of separation is not so successful when the alloy contains a very large quantity of gold, for the latter metal protects the copper and silver from the solvent action of the acid. Thus, if the alloy contains more than $\frac{1}{5}$th of its weight of gold, it is customary to fuse it with a quatity of silver, so as to reduce the proportion of gold below that point before boiling it with the acid. Again, if the alloy contains a large quantity of copper, it is found expedient to remove a great deal of this metal in the form of oxide by heating the alloy in a current of air.

Gold which is brittle and unfit for coining, in consequence of the presence of small quantities of foreign metals, is sometimes refined by melting it with oxide of copper or with a mixture of nitre and borax, when the foreign metals, with the exception of silver, are oxidised and dissolved in the slag. Another process consists in throwing some corrosive sublimate (mercuric chloride) into the melting-pot, and stirring it up with the metal, when its vapour converts the metallic impurities into chlorides, which are volatilised. An excellent method consists in fusing the gold with a little borax, and passing chlorine gas into it through a clay tube. Antimony, arsenic, &c., are carried off as chlorides, whilst the silver, also converted into chloride, rises to the surface of the gold in a fused state, afterwards solidifying into a cake, which is reduced to the metallic state by placing it between plates of wrought-iron and immersing it in diluted sulphuric acid.

When the crude gold is made the anode in an electrolytic cell containing nitric acid, the foreign metals dissolve in the acid while the gold is deposited as a sludge, conveniently caught by surrounding the anode with a bag of cloth. This forms another method of refining gold.

Pure gold, like pure silver, is too soft to resist the wear to which it is subjected in its ordinary uses, and it is therefore alloyed for coinage in this country with $\frac{1}{11}$th of its weight of copper, so that gold coin contains 1 part of copper and 11 parts of gold. The gold used for articles of jewellery is alloyed with variable proportions of copper and silver. The alloy of copper and gold is much redder than pure gold.

The English sovereign contains 91.67 per cent. of gold and 8.33 per cent. of copper. Its sp. gr. is 17.157, and its weight is 123.274 grains.

The Australian sovereign contains silver in place of copper, and is lighter in colour than pure gold.

The degree of purity of gold is generally expressed by quoting it as of so many carats fine. Thus, pure gold is said to be 24 carats fine:

English standard gold 22 carats fine, that is, contains 22 carats of gold out of the 24. Gold of 18 carats fine would contain 18 parts of gold out of the 24, or ¾ths of its weight of gold. The other legal standards are 15, 12, and 9 carat gold. The *fineness* sometimes refers to the quantity of gold in 1000 parts of the alloy; thus, English coin has a fineness of 916.7, German and American coin, of 900.

In order to impart to gold ornaments the appearance of pure gold, they are heated till the copper in the outer layer is oxidised, and then dipped into nitric or sulphuric acid, which dissolves the copper oxide and leaves a film of pure gold.

Pure gold is easily prepared from standard or jeweller's gold by dissolving it in hydrochloric acid mixed with one-fourth of its volume of nitric acid, evaporating the solution to a small bulk to expel excess of acid, diluting with a considerable quantity of water, filtering from the separated silver chloride, and adding a solution of green sulphate of iron, when the gold is precipitated as a dark-purple powder, which may be collected on a filter, well washed, dried, and fused in a small clay crucible with a little borax, the crucible having been previously dipped in a hot saturated solution of borax, and dried, to prevent adhesion of the globules of gold. The action of ferrous sulphate upon the trichloride of gold is explained by the equation—$2AuCl_3 + 6FeSO_4 = Au_2 + F_2Cl_6 + 2Fe_2(SO_4)_3$. The gold precipitated by ferrous sulphate appears, under the microscope, in cubical crystals.

By employing oxalic acid instead of ferrous sulphate, and heating the solution, the gold is precipitated in a spongy state, and becomes a coherent lustrous mass under pressure. The metal is employed in this form by dentists.

When standard gold is being dissolved in *aqua regia*, it sometimes becomes coated with a film of silver chloride which stops the action of the acid; the liquid must then be poured off, the metal washed, and treated with ammonia, which dissolves the silver chloride; the ammonia must then be washed away before the metal is replaced in the acid. In the case of jeweller's gold, it is advisable to extract as much silver and copper as possible by boiling it with nitric acid, before attempting to dissolve the gold. Gold lace should be incinerated to get rid of the cotton before being treated with acid.

The genuineness of gold trinkets, &c., is generally tested by touching them with nitric acid, which attacks them if they contain a very considerable proportion of copper, producing a green stain, but this test is evidently useless if the surface be gilt. The weight is, of course, a good criterion in practised hands, but even these have been deceived by bars of platinum covered with gold. The specific gravity may be taken in doubtful cases; that of sovereign gold is 17.157.

In *assaying gold*, the metal is wrapped in a thin piece of paper together with about three times its weight of pure silver, and added to twelve times its weight of pure lead fused in a bone-ash *cupel* (see p. 465) placed in a muffle (or exposed to a strong oxidising blow-pipe flame), when the lead and copper are oxidised, and the fused oxide of lead dissolves that of copper, both being absorbed by the cupel. When the metallic button no longer diminishes in size, it is allowed to cool, hammered into a flat disc which is annealed by being heated to redness, and rolled out to a thin plate, so that it may be rolled up by the thumb and finger into a *cornette*, which is boiled with nitric acid (sp. gr. 1.18) to extract the silver; the remaining gold is washed with distilled water, and boiled with nitric acid of sp. gr. 1.28, to extract the last traces of silver, after which it is again washed, heated to redness in a small crucible, and weighed.

The stronger nitric acid could not be used at first, since it would be likely to break the cornette into fragments which could not be so readily washed without loss. The addition of the three parts of silver (*quartation*) is made in order to divide the alloy, and permit the easy extraction of the silver by nitric acid, which cannot be effected when the gold predominates.

306. The physical characters of gold render it very conspicuous among the metals; it is the heaviest of the metals in common use, with the exception of platinum, its specific gravity being 19.3. In malleability and ductility it surpasses all other metals; the former property is turned to advantage for the manufacture of gold leaf, for which purpose a bar

of gold, containing 96.25 per cent. of gold, 2.5 per cent. of silver, and 1.25 per cent. of copper, is passed between rollers which extend it into the form of a riband; this is cut up into squares, which are packed between layers of fine vellum, and beaten with a heavy hammer; these thinner squares are then again cut up and beaten between layers of gold-beater's skin until they are sufficiently thin. An ounce of gold may thus be spread over 100 square feet; 282,000 of such leaves placed upon each other form a pile of only 1 inch high. These leaves will allow light to pass through them, and always appear green or blue when held up to the light, though they exhibit the ordinary colour of gold by reflected light.

If a gold leaf adhering to a glass plate be heated to nearly the boiling-point of oil for some time, it becomes nearly transparent and invisible by transmitted light, though still showing the colour of gold by reflected light; if it be pressed with a moderately hard body, it again transmits a green light. When gold wire or leaf is deflagrated by electricity on a glass plate, the finely divided metal transmits ruby, violet, or green light, according to its thickness, though it has the golden colour by reflected light. On heating these deposits to dull redness on the glass, they all change to the ruby colour while still golden by reflection. Pressure with a hard body changes the colour of the transmitted light from red to green. A solution of gold trichloride, containing 0.6 grain of gold in a quart, if shaken with a little solution of phosphorus in ether, in a chemically clean bottle, gives a ruby-red liquid in which the reflected colour of gold may be seen by bringing the solar rays to a focus in the liquid by a convex lens. This liquid will continue to deposit fine particles of gold for many months. The first deposits are blue by transmitted light, and the last are ruby. The supernatant liquid is eventually colourless. If a little sodium chloride be added to the ruby liquid, it transmits a blue light, and the gold which has remained suspended for six months may be deposited in a few hours. By using a filter arranged so that the liquid is passed through the paper in a *radial* instead of an *axial* direction as is usual, the particles of gold, which pass through in ordinary axial filtration, may be collected on the paper, having the various colours, and leaving the liquid colourless. These colours of finely divided gold are taken advantage of in painting upon porcelain, and the well-known magnificent ruby-red glass owes its colour to the same cause. $\frac{1}{10}$th of a grain of gold is capable of imparting a deep rose colour to a cubic inch of fluid.

The extreme ductility of gold is exemplified in the manufacture of gold thread for embroidery, in which a cylinder of silver having been covered with gold leaf it is drawn through a wire-drawing plate and reduced to the thinness of a hair; in this way 6 ounces of gold are drawn into a cylinder two hundred miles in length. Although fusing at about the melting-point of copper, gold is seldom cast, on account of its great contraction during solidification.

Gold is not even affected to the same extent as silver by exposure to the atmosphere, for sulphuretted hydrogen has no action upon it, and hence no metal is so well adapted for coating surfaces which are required to preserve their lustre.

The gold is sometimes applied to the surfaces of metals in the form of an amalgam, the mercury being afterwards driven off by heat. Metals may also be gilt by means of a boiling solution prepared by dissolving gold in *aqua regia*, and adding an excess of bicarbonate of potash or of soda. But the most elegant process of gilding is that of electro-gilding, in which the object to be gilt is connected by a wire with the zinc end of the galvanic battery, and immersed in a solution of cyanide of gold in cyanide of potassium, in which is also placed a gold plate connected with the copper end of the battery, and intended,

by gradually dissolving, to take the place of the gold abstracted from the solution at the negative pole.

A gold crucible is very useful in the laboratory for effecting the fusion of substances with caustic alkalies, which would corrode a platinum crucible. The only single acid which attacks gold is selenic, H_2SeO_4, which the gold reduces to selenious acid, H_2SeO_3. A mixture of hydrochloric with one-third of its volume of nitric acid is usually employed for dissolving gold. It is also dissolved by a mixture of sulphuric acid with a little nitric, the latter becoming reduced to nitrous acid, which precipitates the gold again in the metallic state on pouring the solution into a large volume of water. On account of its high resistance to sulphuric acid, platinum vitriol retorts are now frequently lined with gold. Fused caustic alkalies are not without action on gold, but they attack platinum more strongly.

307. OXIDES OF GOLD.—Three compounds of gold with oxygen have been obtained, Au_2O, AuO, and Au_2O_3, but none of them is of any great practical importance.

Aurous oxide, Au_2O, obtained by decomposing aurous chloride with potash, is a violet-coloured powder which is decomposed by hydrochloric acid—

$$3Au_2O + 6HCl = 2AuCl_3 + 3H_2O + Au_4.$$

Auric oxide, Au_2O_3, is obtained by gently heating *auric hydroxide*, $Au(OH)_3$. This is prepared by heating a weak solution of auric chloride with excess of potash, and adding sodium sulphate, when auric hydroxide is precipitated, of a brown colour like ferric hydroxide. It is very unstable, evolving oxygen when exposed to light. Nitric acid dissolves it, and it is reprecipitated by water. It dissolves in potash, and the solution yields crystals of *potassium aurate*, $KAuO_2.3Aq$. By heating $Au(OH)_3$ at 160° C. AuO is formed.

When precipitated gold is attacked by chlorine gas, it yields *aurous-auric chloride*, $AuCl.AuCl_3$, a dark red hard substance decomposed by water into AuCl and $AuCl_3$, or *auric chloride*, which may also be obtained by dissolving gold in hydrochloric acid with one-fourth of its volume of nitric acid, and evaporating on a water bath to a small bulk; on cooling, yellow prismatic crystals of a compound of the trichloride with hydrochloric acid ($AuCl_3.HCl.4Aq$) are deposited, from which the hydrochloric acid may be expelled by a gentle heat (not exceeding 120° C.), when the trichloride forms red-brown deliquescent crystals of $AuCl_3.2Aq$, dissolving very readily in water, giving a bright yellow solution which stains the skin and other organic matter purple when exposed to light, depositing finely divided gold; the solution appears to contain an acid, H_2AuCl_3O, of which the silver salt is known. Almost every substance capable of combining with oxygen reduces the gold to the metallic state. The inside of a perfectly clean flask or tube may be covered with a film of metallic gold by a dilute solution of the trichloride mixed with citric acid and NH_3, and gently heated. The facility with which it deposits metallic gold, and the resistance of the deposited metal to atmospheric action, has rendered $AuCl_3$ very useful in photography. Alcohol and ether readily dissolve the trichloride, the latter being able to extract it from its aqueous solution. Red crystals of $AuCl_3$ are sublimed when thin gold foil is gently heated in a current of chlorine. Trichloride of gold (like platinic chloride) forms crystallisable compounds with the alkali chlorides and with the hydrochlorides of organic bases, and affords great help to the chemist in defining these last. *Aurochloride of sodium* forms reddish-yellow prismatic crystals ($NaCl.AuCl_3.2Aq$), which are sold for photographic purposes.

Protochloride of gold, or *aurous chloride* (AuCl), is obtained by gently heating the trichloride, when it fuses and is decomposed at 177° C., leaving the protochloride, which is reduced to metallic gold at about 205° C. Aurous chloride is sparingly soluble in water, and of a pale yellow colour. Boiling water decomposes it into metallic gold and the trichloride.

Fulminating gold is obtained as a buff precipitate when ammonia is added to solution of auric chloride; its composition is not well established, but appears to be $Au_2O_3.4NH_3$ or $2(NH_3.NAu'').3H_2O$. It explodes violently when gently heated.

The *Sel d'or* of the photographer is a hyposulphite (thiosulphate) of gold and

sodium, $Au_2S_2O_3.3Na_2S_2O_3.4Aq$, which is obtained in fine white needles by pouring a solution of 1 part of auric chloride into a solution of 3 parts of sodium hyposulphite, and adding alcohol, in which the double salt is insoluble. Its formation may be explained by the equation—

$$8Na_2S_2O_3 + 2AuCl_3 = Au_2S_2O_3.3Na_2S_2O_3 + 6NaCl + 2Na_2S_4O_6.$$

It is doubtful whether the above formula represents the true constitution of this salt, for it is not decomposed by acids in the same manner as ordinary thiosulphates are.* HNO_3 separates all the gold in the metallic state.

Purple of Cassius, which is employed for imparting a rich red colour to glass and porcelain, is a compound of gold, tin, and oxygen, which are believed to be grouped according to the formula $Au_2SnO_3.Sn.SnO_3.4Aq$.† It may be prepared by adding stannous chloride to a mixture of stannic chloride and auric chloride; 7 parts of gold are dissolved in *aqua regia* and mixed with 2 parts of tin also dissolved in *aqua regia*; this solution is largely diluted with water, and a weak solution of 1 part of tin in hydrochloric acid is added, drop by drop, till a fine purple colour is produced. The purple of Cassius remains suspended in water in a very fine state of division, but subsides gradually, especially if some saline solution be added, as a purple powder. The fresh precipitate dissolves in ammonia, but the purple solution is decomposed by exposure to light, becoming blue, and finally colourless, metallic gold being precipitated, and stannic oxide left in solution.

The *sulphides of gold* are not thoroughly known. Gold does not combine directly with sulphur, but if it be heated with sulphur and alkali sulphides, it forms soluble compounds. In this way, *sodium auroxulphide*, $NaAuS.4Aq$, may be obtained in colourless prisms soluble in alcohol. When H_2S is passed into solution of $AuCl_3$, a black precipitate of $Au_2S.Au_2S_3$ or Au_2S_2 is obtained—

$$2AuCl_3 + 3H_2S = Au_2S_2 + S + 6HCl.$$

The precipitate is soluble in alkali sulphides. The precipitated sulphide of gold is not dissolved by the acids, with the exception of *aqua regia*. Nitric acid oxidises the sulphur, leaving metallic gold. When hydrosulphuric acid is added to a boiling solution of auric chloride, the metal itself is precipitated—

$$8AuCl_3 + 3H_2S + 12H_2O = Au_8 + 24HCl + 3H_2SO_4.$$

A yellowish-grey brittle *arsenide of gold* ($AuAs_2$) has been found in quartz in Australia.

* It appears to be *sodium aurothiosulphate*, $Na_3AuS_4O_6.2Aq$, which is supported by the preparation of a corresponding barium salt and by decomposing this with sulphuric acid when *aurothiosulphuric acid*, $H_3AuS_4O_6$, is obtained.

† Debray asserts that it is merely a mixture of precipitated gold and stannic hydrate.

ORGANIC CHEMISTRY.

308. The division of chemistry into inorganic and organic was originally intended to distinguish mineral substances from those derived from animal and vegetable life; but since many of the latter may now be produced in the laboratory from the elements obtainable from mineral sources, it has become usual to define organic chemistry as the chemistry of the compounds of carbon, since this element is always present in the substances formerly spoken of as organic.

Organic chemistry differs from inorganic in being chiefly concerned with the compounds produced by the arrangement, in different proportions or in different positions, of the elements carbon, hydrogen, oxygen, and nitrogen, though the other elements occasionally enter into the composition of organic compounds.

Perhaps the most striking difference between compounds of carbon and those of other elements is the large number of atoms contained in one molecule of the majority of carbon compounds. So far as evidence is available it is rare in inorganic chemistry to find a compound whose molecule contains so many as six atoms of any one element; yet the majority of carbon compounds contain more than six atoms of carbon in the molecule, so that it would appear to be a characteristic property of carbon to combine with itself.

A useful practical distinction between organic and inorganic substances is afforded by their behaviour when heated. An organic substance is either converted into vapour when moderately heated, or decomposed into volatile products, generally leaving a residue of charcoal, which burns away when heated in air.

Upon this is based the *ultimate analysis of organic compounds* for the purpose of ascertaining the relative proportions of their elements.*

The *making a combustion*, as it is technically called, consists in burning the organic compound so as to convert its carbon into CO_2 and its hydrogen into H_2O, from the weight of which the proportions of those elements are obtained by calculation. The substance to be analysed, having been carefully dried and weighed (about 0.5 gram), is placed in a small boat-shaped tray of porcelain or platinum, which is introduced into one end of a glass tube about 30 inches long, of which about 24 inches are filled with small fragments of carefully dried cupric oxide. The end of the tube where the boat is placed is connected with an apparatus for transmitting air or oxygen, which has been purified from CO_2 by passing through potash, and from H_2O by calcium chloride. To the other end of the tube is attached, by a perforated cork, a weighed tube (B) filled with small fragments of calcium chloride to absorb H_2O, and to this is joined, by a caoutchouc tube, a *bulb-apparatus* (C) containing strong potash to absorb CO_2, and a small *guard-tube*

* For exact details of the methods of organic analysis the reader must consult works on analytical chemistry.

with calcium chloride to prevent loss of water from the potash. The *potash-bulbs* and guard tube are accurately weighed. The *combustion-tube* is supported in a gas-furnace, and that portion which contains the CuO is heated to redness. The end containing the boat is then gradually heated, so that the organic substance is slowly vaporised or decomposed. The vapour or the products of decomposition, in passing over the red-hot cupric oxide, will acquire the oxygen necessary to

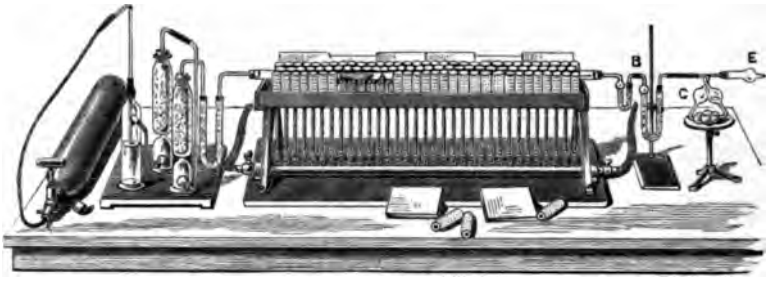


Fig. 245.—Apparatus for organic analysis.

convert the C into CO_2 and the H into H_2O, which are absorbed in the potash bulbs and calcium-chloride tube. At the end of the process, which commonly occupies about an hour, a slow stream of pure air or oxygen is passed through, whilst the entire tube is red-hot, in order to burn any charcoal which may remain in the boat, and to carry forward all the CO_2 and H_2O into the absorption apparatus. The weight of the CO_2 is given by the increase in weight of the calcium chloride.

When nitrogen is present in the substance, it may be partly converted into NO_2, which would increase the weight of the absorption-apparatus. To avoid this, three or four inches of the front end of the combustion-tube are filled with metallic copper, which, being heated to redness, absorbs the O from the NO_2, leaving N, which passes through the absorption-apparatus and escapes. When it is desired to make a *determination of the nitrogen*, the combustion-tube is arranged in the same way, but the absorption-apparatus is exchanged for a bent tube to permit the collection of the gas in a measured tube filled with strong potash. Before commencing the combustion, the air is swept out of the tube by a stream of pure CO_2, which is continued during the combustion, and is absorbed by the potash, the nitrogen being collected and measured.

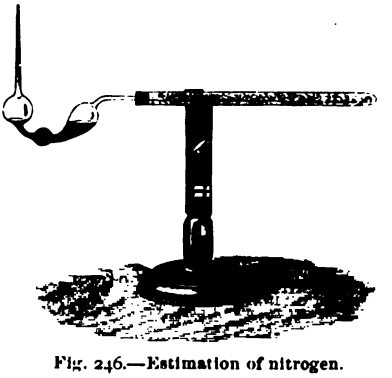


Fig. 246.—Estimation of nitrogen.

Another method of estimating nitrogen in organic substances consists in heating them with *soda-lime*, when the N is evolved as NH_3, which is absorbed by hydrochloric acid in the absorption bulb shown in Fig. 246, and precipitated by platinic chloride, the weight of N being calculated from that of the $PtCl_4.2NH_4Cl$ obtained: or the NH_3 is absorbed in a known quantity of acid which is afterwards titrated with a standard solution of alkali, and the quantity which has been neutralised by the evolved ammonia thus determined.

Kjeldahl's method of estimating nitrogen consists in oxidising the substance by heating it with H_2SO_4 and acid potassium sulphate ($KHSO_4$), whereby the N is converted into NH_3, which forms ammonium sulphate. The NH_3 is subsequently liberated by boiling with alkali, absorbed by hydrochloric acid and determined either with platinic chloride or standard alkali, as described above.

Sulphur and *phosphorus* are estimated in organic compounds by converting

them into sulphuric and phosphoric acids, respectively, by the action of powerful oxidising-agents (nitric acid, chloric acid, bromine, &c.), and determining these acids by the usual methods. The *halogens* are determined by oxidising the substance by heating it with strong HNO_3 under pressure, whereby the halogen is converted into its hydrogen compound and may be precipitated by $AgNO_3$ and weighed as silver halide.

The proportion of *oxygen* in an organic substance is generally ascertained by difference, that is, by deducting the sum of the weights of all the other elements from the total weight of the substance.

As an example of the ultimate analysis of an organic compound, that of alcohol may be given (volatile liquids are weighed in a small glass bulb with a thin stem, the end of which is sealed for weighing, and broken off when the bulb is introduced into the combustion-tube):—

.5 gram alcohol, burnt with cupric oxide, as above, gave .9565 gram CO_2 and .5869 gram H_2O.

Since 44 grams CO_2 contain 12 grams C., $\frac{12}{44}$ of .9565, or .2608, is the weight of C found.

Since 18 grams H_2O contain 2 grams H, $\frac{2}{18}$ of .5869, or .0652, is the weight of H found.

The sum of C and H is .2608 + .0652, or .3260. Deducting this from .5 gram alcohol, we have .174 gram for the weight of O contained in it.

So that .5 gram alcohol contains—

.2608 gram carbon	or 52.16	per cent.
.0652 „ hydrogen	.. 13.04	„
.1740 „ oxygen	„ 34.80	„

It is usual to express the results of such an analysis in an *empirical formula*, which gives, in the simplest form, the relative number of atoms of the elements present.

309. *To deduce the empirical formula from the percentage composition*, the percentage of each element is divided by its atomic weight, and the ratio of the resulting quotients expressed in its lowest terms; thus—

52.16	divided by 12	gives	4.34	atomic weights of	carbon
13.04	.. 1	..	13.04	.. ..	hydrogen
34.80	.. 16	„	2.17	.. ..	oxygen

If the ratio 4.34 : 13.04 : 2.17 be expressed in its lowest terms, it becomes 2 : 6 : 1, giving for the *empirical formula* of alcohol, C_2H_6O.

The question now arises whether this formula is a true representation of the molecule or indivisible particle of alcohol, or whether the molecule should be written $C_4H_{12}O_2$, or $C_6H_{18}O_3$, or in any other form which would preserve the ratio established beyond dispute by the above analysis.

310. *To deduce the molecular formula of a compound from its empirical formula* the molecular weight of the compound must be determined, for it is evident that the formula C_2H_6O represents 2 atoms of C, weighing 12 × 2, 6 atoms of H, weighing 1 × 6, and 1 atom of O, weighing 16; the sum of these numbers, or 46, would be the weight of alcohol represented by C_2H_6O, whereas the formula $C_4H_{12}O_2$ would express 46 × 2 parts by weight, and $C_6H_{18}O_3$ would express 46 × 3 parts by weight of alcohol.

The methods for determining the molecular weight of a volatile compound have been described at p. 292.

In the case of a substance which cannot be converted into vapour without decomposition, the molecular weight is determined by the cryoscopic method (p. 319), or is inferred from a consideration of the chemical relations of the substance, and its determination is sometimes a difficult matter. The general character of the latter method will be seen from the following examples:

Determination of the molecular formula of an acid.- The substance yielded, on combustion with cupric oxide, in 100 parts—carbon, 40, hydrogen, 6.66, oxygen 53.33; which lead to CH_2O as the simplest or empirical formula of the acid.

The acid was found to give only one class of salts with K and Na, showing that it only contains one atom of H exchangeable for a metal, or is monobasic (p. 104).

By neutralising the acid with ammonia, and stirring with solution of silver nitrate, a crystalline silver salt was obtained, which was purified by recrystallisation from hot water, dried, weighed in a porcelain crucible of known weight, and gradually heated to redness. On again weighing the crucible after cooling, it was found to contain a quantity of metallic silver amounting to 64.66 per cent. of the weight of the salt. Now, as a general rule, a silver salt is formed from an

acid by the displacement of an atom of hydrogen by an atom of silver; so that what remains of a silver salt, after deducting the silver, represents the acid itself *minus* a quantity of hydrogen equivalent to the silver.

From the silver salt	100.00
Deduct the silver	64.66
Acid residue	35.34

Then 64.66 Ag : 108 { *Ag in one molecule of the salt* } : : 35.34 : 59 { *acid residue in one molecule,*

To the acid residue	59
Add the hydrogen equivalent to an atom of Ag	1
Molecular weight of the acid . .	60

The formula CH_2O represents $12+2+16=30$. Hence the molecular formula is $C_2H_4O_2=60$; and the silver salt is $C_2H_3AgO_2$.

Determination of the molecular formula of an organic base.—The substance yielded on combustion with cupric oxide, in 100 parts, carbon 77.42, hydrogen 7.53. A determination of nitrogen gave 15.05 per cent., so that there was no oxygen. These numbers lead to C_6H_7N as the simplest or empirical formula of the base. By dissolving the base in hydrochloric acid and adding platinic chloride, a yellow crystalline precipitate was obtained, resembling the ammonio-platinic chloride formed when ammonia is treated in the same way. This precipitate was washed with alcohol, dried, weighed in a porcelain crucible, and heated to redness, when it left a residue of metallic platinum, which amounted to 32.72 per cent. of the weight of the salt. As a general rule, a platinum-chloride salt is formed by the combination of $PtCl_4$ with two molecules of the hydrochloride of the base; in the case of the ammonio-platinic chloride, the formula is $PtCl_4.2(NH_3.HCl)$; so that what remains of a platinum salt after deducting the platinum represents two molecules of the base + two molecules of HCl + 4 atoms of chlorine.

From the platinum salt . . .	100.00
Deduct the platinum . .	32.72
Remainder	67.28

Then 32.72 Pt : 195 { Pt in one molecule of the salt } : : 67.28 : 400.9

Hence two mols. base + 2 mols. HCl + 4 atoms Cl =	400.9
Deduct $2HCl+Cl_4$	= 215.0
Weight of two molecules of the base .	185.9

The molecular weight of the base, therefore, is 92.9. The formula C_6H_7N represents $72+7+14=93$. This is therefore the molecular formula.

The *law of even numbers* is sometimes a useful guide in fixing molecular formulæ. It may be thus expressed: *The total number of atoms of monad or triad elements united with carbon in an organic compound must be an even number.* The law is a result of the tetrad nature of carbon, as will be seen in the next few pages.

For example, the empirical formula for glycol, deduced from ultimate analysis, is CH_3O; but this is an impossible formula, by the law of even numbers, and the molecular formula for glycol must be at least double this, $C_2H_6O_2$.

311. The ultimate analysis of an organic compound serves to decide its *empirical formula—i.e.*, the formula expressing the ratio between the number of atoms of each element in the compound; a determination of the molecular weight decides whether the *molecular formula* (*i.e.*, the formula expressing the actual number of atoms of each element in one molecule of the compound) is identical with, or a multiple of, the empirical formula. Thus, the empirical formula for benzene is CH, but its molecular formula is undoubtedly six times this—viz., C_6H_6.

From what was said in the chapter on nitrogen, and again on p. 191, it will be apparent that much light may be thrown upon the behaviour of compounds by a study of the way in which the component atoms are

combined together. In this manner the existence of *radicles* in compounds can be traced, and it becomes possible to assign a *constitutional* or *rational formula—i.e.*, a formula which indicates the radicles that compose it—to a compound. Furthermore, it becomes necessary, in the case of carbon compounds, to provide some working hypothesis which shall account for the fact that many substances exist which have different properties, but nevertheless have the same ultimate composition and the same molecular formula: such cases are included under the term *isomerism*, which will shortly receive closer attention. The necessary hypothesis is supplied by supposing the atoms in the compound to be linked together by *bonds* in such a way that this linkage can be represented by a *graphic* or *structural formula* on one plane, as explained on p. 101.

It is only by such a study of the *structure* of carbon compounds that any success has been achieved in the main object of chemistry, namely, the synthesis of compounds. The study involves a careful consideration of the reactions of the compound, and many examples will be met with hereafter; the following may, however, be now quoted as a typical simple case.

312. *Example.—Determination of the rational or structural formula of alcohol.* When sodium is placed in alcohol, it is dissolved with the evolution of much hydrogen, and the alcohol is converted into a crystalline substance called sodium ethoxide, which has the composition C_2H_5ONa. Comparing this with the formula of alcohol, it is seen that Na has been substituted for one atom of H. Since the compound still contains H_5, it might be supposed that by the use of an excess of Na more might be substituted for H, producing ultimately a compound C_2Na_6O. But this is not the case: Na can be substituted in this way for only one of the 6 atoms of H in alcohol; hence it is seen that one atom of the six is on a different footing from the other five. This would be expressed by writing the formula C_2H_5OH.

Again, when alcohol is acted on by hydrogen chloride, and distilled at a low temperature, it yields water and a very volatile liquid known as ethyl chloride, having the composition C_2H_5Cl. This decomposition would be expressed by the equation, $C_2H_5OH + HCl = C_2H_5Cl + HOH$, from which it is evident that the Cl of the HCl has been exchanged for OH in the alcohol, leading to the conclusion that alcohol is made up of at least two separate groups, and that one way of writing its rational formula is $C_2H_5{\cdot}OH$.

313. By investigating the nature of the radicles contained in an organic substance, this may generally be assigned to one of the following divisions:

(1) HYDROCARBONS, composed of carbon and hydrogen only, in various modes of grouping; as *ethyl hydride* or *ethane*, $C_2H_5{\cdot}H$.

Hydrocarbons from which hydrogen has been removed give rise to *hydrocarbon radicles*, thus, C_2H_5 is the hydrocarbon radicle, *ethyl*, from ethane; like all other radicles they are incapable of a separate existence (p. 94). Since in chemical reactions the hydrocarbon radicles behave towards other radicles analogously to the manner in which the metals behave towards the non-metals, they are frequently termed *positive radicles*, other radicles such as (OH),(COOH), etc., being termed *negative*.

(2) ALCOHOLS, composed of carbon, hydrogen, and oxygen, and containing one or more *hydroxyl* (OH) radicles; as *ethyl-alcohol*, $C_2H_5{\cdot}OH$.

(3) ALDEHYDES, or dehydrogenated alcohols; products of the partial oxidation of the alcohols, containing the group (COH); as *ethyl-aldehyde*, $CH_3{\cdot}COH$.

(4) ACIDS, the products of the further oxidation of the alcohols,

containing one or more *carboxyl* radicles, CO_2H; as *acetic acid*, $CH_3{\cdot}CO{\cdot}OH$ or $CH_3{\cdot}CO_2H$.

(5) KETONES, formed from the acids by the substitution of a hydrocarbon radicle for the OH in the carboxyl; so that the ketones contain the group CO; as *acetic ketone* or *acetone*, $CH_3{\cdot}CO{\cdot}CH_3$.

(6) ETHERS, formed from the alcohols by the substitution of a hydrocarbon radicle for the H in the hydroxyl, as *ethyl-ether*, $C_2H_5{\cdot}O{\cdot}C_2H_5$.

(7) HALOID COMPOUNDS, formed from the foregoing groups by the substitution of a halogen radicle for hydrogen or hydroxyl; as *chloroform*, $CHCl_3$; *ethyl chloride*, C_2H_5Cl; *acetyl chloride*, $CH_3{\cdot}CO{\cdot}Cl$.

(8) ETHEREAL SALTS (or *esters*), formed from the acids by the substitution of a hydrocarbon radicle for the hydrogen in the carboxyl radicle; as *ethyl acetate*, $CH_3{\cdot}CO{\cdot}OC_2H_5$.

(9) ORGANO-MINERAL COMPOUNDS, formed upon the type of the chlorides of metals or non-metals by the substitution of hydrocarbon radicles for the chlorine; as *zinc ethide*, $Zn(C_2H_5)_2$.

(10) AMMONIA-DERIVATIVES, formed upon the model of ammonia, NH_3, by the substitution of a radicle for hydrogen; as *ethylamine*, $NH_2{\cdot}C_2H_5$, *acetamide*, $NH_2{\cdot}C_2H_3O$.

(11) CYANOGEN COMPOUNDS, containing the group CN; as *hydrocyanic acid*, $H{\cdot}CN$.

(12) PHENOLS, resembling the alcohols in composition, by containing the hydroxyl group, but resembling the acids in some of their properties, and not yielding aldehydes when partially oxidised; as *phenol*, $C_6H_5{\cdot}OH$.

(13) QUINONES, formed from hydrocarbons by the substitution of a group of two oxygen atoms for two hydrogen atoms; as *quinone*, $C_6H_4(O_2)$, from benzene, C_6H_6.

Compounds for which sufficient evidence of a rational formula has not been obtained are classified according to similarity in properties, ultimate composition, or products of decomposition. The following are the most important of such classes:

(14) CARBOHYDRATES, or compounds containing six, or some multiple of six, atoms of carbon, together with some multiple of the group H_2O; as *starch*, $C_6H_{10}O_5$, *glucose*, $C_6H_{12}O_6$, *sugar*, $C_{12}H_{22}O_{11}$.

(15) GLUCOSIDES, or compounds which yield glucose as one of their products of decomposition; as *salicin*, $C_{13}H_{18}O_7$.

(16) ALBUMINOIDS and GELATINOIDS, or compounds containing C, H, N, and O, often with small quantities of S, and sometimes of P, distinguished by their tendency to putrefy when moist; *albumin*, *fibrin*, and *casein* are examples of such compounds, but they cannot at present be represented by satisfactory formulæ.

(17) HETEROCYCLIC COMPOUNDS.—The nature of these will be explained later.

With few exceptions, one or other of the typical formulæ cited in the foregoing classification contains a hydrocarbon radicle; it is, indeed, possible to build up the members of each group by starting with one or other of the hydrocarbons. Hence, nearly all organic compounds are either hydrocarbons or *hydocarbon derivatives*.

In 1813 Chevreul showed that a fat is composed of glycerine and a *fatty acid*, and in 1848 Kolbe obtained hydrocarbons by electrolysing salts of fatty acids. Later the aromatic substances, like the essential oils and balsams, were studied and

found to yield hydrocarbons richer in carbon than those obtainable from the fatty compounds. A classification of hydrocarbons into a *fatty** and an *aromatic* series was a natural consequence. But in the advance of a science definitions become blurred by more accurate knowledge, and, for a reason which will be apparent later, the terms *open-chain* and *closed-chain* (or *acyclic* and *cyclic*) have been adopted as more accurately expressing the differences implied by the words fatty and aromatic respectively. Even this division is losing its aptness, for bodies of fatty nature have been detected among closed-chain compounds. For this reason no actual division is made in the following pages.

HYDROCARBONS.

314. As will be explained, these are either *saturated* or *unsaturated*, accordingly as they behave towards chemical agents.

Saturated Hydrocarbons.

Paraffin Series of Hydrocarbons.—The only hydrocarbon which contains one atom of carbon is *methane* or *marsh gas*, CH_4, the more important properties of which have been already considered.

It has been seen that when CH_4 undergoes metalepsis with chlorine, one of its H atoms is exchanged for Cl, the compound CH_3Cl being produced (p. 174). Now there are several other methods of producing a compound of this formula, and, whichever be adopted, the product always has the same properties, showing that *only one compound of the formula* CH_3Cl *exists*. It is contrary to experience, acquired in other cases, to suppose that all the methods of producing CH_3Cl would result in the substitution of Cl for the same H atom, and it may be fairly inferred that whilst one method would produce CHHHCl, another would produce CHHClH, a third CHClHH, and a fourth CClHHH. In each case the substance produced is the same. It is therefore supposed that all the four H atoms in methane have an equal position with regard to the carbon atom, so that whichever is substituted the centre of gravity of the molecule will remain the same.

It is in order to express, or to attempt to explain, this equality of position of the hydrogen atoms in relation to the carbon, that they are often represented on paper as symmetrically arranged round the centre carbon atom (Fig. 247), so that whichever H is exchanged for Cl, the figure has only to be turned round in order to appear the same. On paper the atoms are, of necessity, written on the same plane, but it is not to be supposed that this represents their arrangement in the molecule. At present we have no satisfactory knowledge of the shapes of molecules, but we are obliged to think of them as having three dimensions. The most fruitful hypothesis as to the structure of the methane molecule is that the carbon atom occupies the centre of a regular tetrahedron, the hydrogen atoms being attached to the four angles thereof.

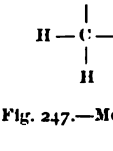


Fig. 247.—Methane.

Inasmuch as methane has the formula CH_4, generally written as in Fig. 247, it must be regarded as a *saturated compound* devoid of any residual affinity such as that possessed by CO (p. 136).

In the case of all other hydrocarbons it is assumed that the carbon atoms are directly united together, since it does not appear to be possible for H to behave other than as a monovalent element, so that it cannot be supposed to act as an intermediary, that is, in a manner represented by the expression C-H-C. Of those hydrocarbons which have two carbon atoms, or a two-carbon *nucleus*, there are at least three, of which two, ethylene, C_2H_4, and acetylene, C_2H_2, have received notice (pp. 142 and 137) and will be referred to again. The third is called *ethane*, and has

* Attempts have been made to substitute *aliphatic* for fatty.

the formula C_2H_6, which is generally represented as shown in Fig. 248, but is equally well written $H_3C{\cdot}CH_3$.

The evidence for this formula is of a similar character to that for the methane formula, only one compound C_2H_5Cl being obtainable. If two regular tetrahedra be placed with one solid angle of each in contact, a two-carbon nucleus will be represented in which each carbon is at the centre of a tetrahedron, the six H atoms being at the remaining three angles of each tetrahedron (see Fig. 257).

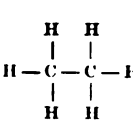


Fig. 248.—Ethane.

Ethane is also a saturated hydrocarbon, for all the bonds of the two carbon atoms are satisfied. Passing to those hydrocarbons which contain three carbon atoms, or a three-carbon nucleus, that which is saturated, and therefore contains the highest number of hydrogen atoms, is C_3H_8, called *propane*, and is represented as in Fig. 249, or more simply as $CH_3{\cdot}CH_2{\cdot}CH_3$.

The evidence for this formula is derived from the methods by which propane is prepared, and will be appreciated when these are described. The reasoning applied to methane will not serve in this case, for two compounds of the formula C_3H_7Cl are known, as will be explained later.

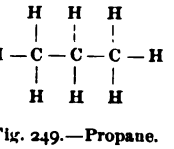


Fig. 249.—Propane.

A comparison of these three hydrocarbons will show that ethane may be regarded as derived from methane, and propane from ethane, by substituting CH_3 for H. By continuing this process a whole series of hydrocarbons is obtained, each of which is saturated and differs from the one preceding it by CH_2. Thus *butane*, the next member of the series, is $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$, *pentane* is $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$, and so on. Any series of carbon compounds, each member of which differs from the one preceding it by CH_2, is called an *homologous series*, and the compounds are *homologues* of each other.

It will be seen that in the homologous series under consideration, the number of hydrogen atoms must always exceed twice the number of carbon atoms by 2, and that a *general formula* for the series may therefore be written C_nH_{2n+2}. Since each terminal carbon atom has three hydrogen atoms attached to it, the general formula may be extended to $H_3C{\cdot}C_nH_{2n}{\cdot}CH_3$. As already stated, hydrocarbons which conform with this general formula are termed *saturated* because they cannot have any free affinities by which other elements can attach themselves to the molecule. It must be understood that this title does not represent a mere theoretical speculation, but is the expression of actual experience, since it is found to be impossible to produce a new compound from any of these hydrocarbons save by *substitution*; for example, no compound containing chlorine can be obtained from methane except by *exchanging* one or more atoms of Cl for one or more atoms of H. On account of this inactivity the series has been called the *paraffin series* of hydrocarbons, the name paraffin (*parum*, little, *affinis*, affinity) having been originally bestowed upon the wax-like substance obtained in the distillation of coal and peat, because of its resistance to chemical agents; this solid was subsequently shown to consist mainly of saturated hydrocarbons.

The paraffin hydrocarbons may be regarded as the hydrides of positive radicles of the general formula C_nH_{2n+1}, the formula for the hydrocarbons being $C_nH_{2n+1}H$. These radicles have been termed *alkyl*

radicles; they are obviously monovalent. They are designated similarly to the hydrocarbons which constitute their hydrides, the suffix *-yl* being substituted for *-ane*.

The natural source of the paraffin hydrocarbons is the oil known as *petroleum, mineral naphtha,* or *rock-oil.* This is found in nearly all countries, but especially at Baku, on the Caspian Sea, and in Canada and Pennsylvania, and occurs in almost all geological formations. It is to be noted, however, that the Russian petroleum consists largely of hydrocarbons (naphthenes) allied to the aromatic series (*q.v.*), whilst that of Pennsylvania consists almost entirely of a mixture of paraffin hydrocarbons.

The Pennsylvanian *oil-wells* discharge large volumes of gas containing H, CH_4, and C_2H_6, which are used for heating and lighting in the neighbouring district. The liquid pumped out of the wells still retains a quantity of ethane in solution. It consists chiefly of members of the paraffin series, of which a list is here given—

Methane	CH_4	Gas			Boils at
Ethane	C_2H_6	,,	Heptane	C_7H_{16}	98° C.
Propane	C_3H_8	,,	Octane	C_8H_{18}	125°
Butane	C_4H_{10}	,,	Nonane	C_9H_{20}	149°
		Boils at	Decane	$C_{10}H_{22}$	173°
Pentane	C_5H_{12}	36° C.	Dodecane	$C_{12}H_{26}$	214°
Hexane	C_6H_{14}	69°	Hexadecane	$C_{16}H_{34}$	287°

The liquid constituents of the petroleum are separated by the process of *fractional distillation*, which depends upon the difference in their boiling-points.

When the petroleum is heated, the hydrocarbons, ethane, propane, and butane, are evolved in the gaseous state; these are collected and subjected to the action of a condensing pump, which liquefies a portion of them, yielding the liquid sold as *cymogene* (sp. gr. 0.59), which is used in freezing-machines, on account of the cold produced by its rapid evaporation. It consists chiefly of butane, C_4H_{10}.

The portion which first distils over requires special condensation, for it boils at 18° C.; it contains a considerable proportion of pentane, and is sold as *rhigolene* (sp. gr. 0.62), being used as an anæsthetic, and for a standard of light. The portion which distils over about 60° C. consists mainly of hexane, and is sold as *petroleum spirit, petroleum ether,* or *gasolene* (sp. gr. 0.66); it is used for dissolving india-rubber. The next fraction is chiefly heptane, and is collected until the temperature rises to 110° C.; its sp. gr. is 0.7, and it is used, in some kinds of lamps, as a burning oil, and as a solvent, under the names *naphtha, ligroin,* and *benzoline.* The next fraction is collected below 150° C., and is known as *benzine* (sp. gr. 0.74), a solvent which must not be confounded with *benzene*, the coal-tar product. A similar fraction is the *petrol* burnt in the engines of motor-cars. The *kerosene oil*, so much in use for paraffin lamps, is the portion which distils between 150° and 300° C., and is generally refined by agitation with about 2 per cent. of sulphuric acid (which removes the olefines contained in the oil) before being sent into the market. It is unsafe to use oils of low boiling-point as illuminants in ordinary lamps, because they so easily evolve vapour, which forms an explosive mixture with air, and bursts the lamp.

The temperature at which the hydrocarbon evolves enough vapour to form an inflammable mixture with the air above it is termed its *flashing-point.* No paraffin oil is considered safe for burning, in England, which kindles from a flame brought near to its surface when it is heated to 38° C. (100° F.) *in an open vessel*; a teacup placed in a basin of hot water in which a thermometer is plunged, answers for a rough test. In a closed vessel, where the vapour more rapidly accumulates in sufficient quantity, the flashing-point is much lower, and no oil is considered safe which kindles at or below 23° C. (73° F.) in a covered vessel when a flame is brought near its surface; a small beaker covered with a piece of tin

plate having a small hole for introducing a match, may be placed in warm water for the *close test*.

The distillation of the petroleum is finally pushed until a tarry residue is left in the retort. The distillate above 300° C. consists of heavy (sp. gr. 0.9) *lubricating oils* containing *paraffin-wax*, which melts at about 55° C., and may, therefore, be separated from the oils by freezing; this wax contains the highest known homologues of the paraffin series. The softer varieties of paraffin are known as *vaseline*.

Ozokerite, a crude form of which is known as *ceresin*, is imported from Galicia, Hungary, and Russia, for the manufacture of candles. It consists of solid hydrocarbons which appear to contain a smaller proportion of hydrogen than do the paraffin hydrocarbons; its melting-point varies from 60° C. to 100° C.

Paraffin oils, both illuminating and lubricating, and paraffin-wax are also obtained by distilling certain minerals allied to coal, such as the Torbane Hill mineral, or *Boghead cannel*, found at Bathgate, in Scotland. Such *shale oils* contain more olefines than do the American oils.

All the oils above mentioned are colourless when quite pure, although the commercial products are frequently yellow or brown.

315. On the small scale, the process of fractional distillation for the separation of liquids of different boiling-points is conducted in a flask (A, Fig. 250) provided

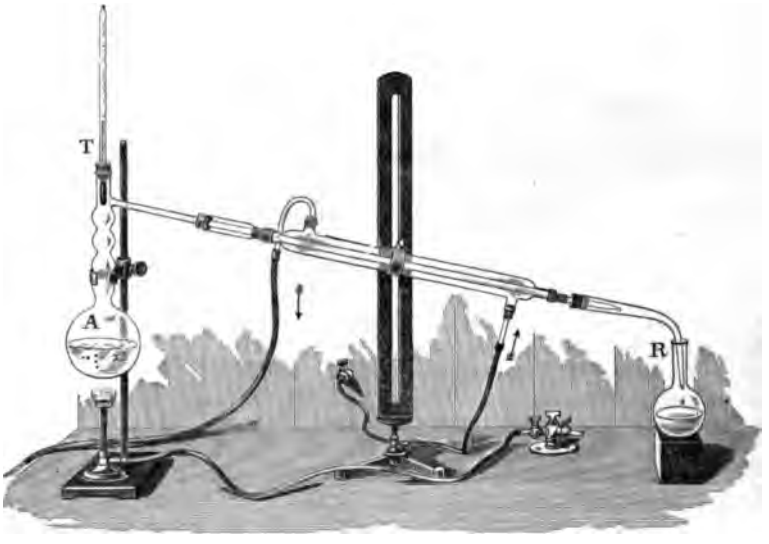


Fig. 250.—Fractional distillation.

with a long neck through which a thermometer (T) passes to indicate the temperature at which the liquid boils. The first portion which distils over will, of course, consist chiefly of that liquid which has the lowest boiling-point, particularly if the neck of the flask consist of a series of bulbs and thus expose a large surface to be cooled by the air: if the receiver (R) be changed at stated intervals corresponding with a certain rise in the temperature, a series of liquids will be obtained, containing substances the boiling-point of which lie within the limits of temperature between which the liquids were collected.

When these liquids are again distilled separately in the same way, a great part of each is generally found to distil over within a few degrees on either side of some particular temperature, which is the boiling-point of the substance of which that liquid chiefly consists; and if the receivers be again changed at stated intervals, a second series of distillates will be obtained, the boiling-points of which are comprised within a narrower range of temperature. It will be evident that, by repeated distillations, the original mixture will eventually be resolved

into a number of liquids, each distilling over entirely at about one particular temperature, which is the boiling-point of its chief constituent.

316. **Methane**, or *methyl hydride*, CH_4. The following must be added to the description of methane which has already been given (p. 144).

To prepare the pure gas, methyl iodide is dropped slowly into a flask *A* (Fig. 251) containing a copper-zinc couple (p. 21) covered with dilute alcohol; the flask is very gently heated, whereupon methane is evolved in accordance with the equation — $CH_3I + C_2H_5OH + Zn = CH_3H + ZnI.OC_2H_5$, and passes up the tube *B* containing granulated zinc which decomposes any unchanged CH_3I, allowing the methane to be collected in the usual manner from the delivery tube. Methane is also formed when zinc methide is decomposed by water, $Zn(CH_3)_2 + 2HOH = Zn(OH)_2 + 2CH_4$, and by the action of sodium amalgam and water (to supply H) on carbon tetrachloride, $CCl_4 + H_8 = CH_4 + 4HCl$, and by passing a mixture of CS_2 vapour and H_2S (or steam) over red-hot copper, $CS_2 + 2H_2S + Cu_8 = 4Cu_2S + CH_4$. The last two methods are of great importance, since they amount to the preparation of the gas from its elements, and, therefore, to the synthesis of the paraffin hydrocarbons generally, for the majority of these can be built up from marsh-gas by the aid of a few elements which act as intermediaries.

Fig. 251.—Preparation of methane.

Methane is nearly inodorous; its sp. gr. is 0.56 (air = 1); it burns with a feebly luminous flame; water dissolves about 5 per cent., and alcohol 50 per cent. of the gas. It boils at -160° C., but is liquid at -11° C., under 180 atmospheres pressure; the sp. gr. of the liquid is 0.415 at -164° C.

When methane is mixed with chlorine and exposed to sunlight, a violent reaction occurs, and often an explosion, HCl being formed, and C separated; but when the Cl is diluted with CO_2 and allowed to act gradually, *chlorine substitution-products* are obtained.

$CH_4 + Cl_2 = HCl + CH_3Cl$ *monochloromethane.*
$CH_4 + 2Cl_2 = 2HCl + CH_2Cl_2$ *dichloromethane.*
$CH_4 + 3Cl_2 = 3HCl + CHCl_3$ *chloroform.*
$CH_4 + 4Cl_2 = 4HCl + CCl_4$ *tetrachloromethane.*

The chlorine in these compounds is not precipitated by silver nitrate, like the Cl in HCl and the chlorides of the metals.

Ethane, or *ethyl hydride*, C_2H_6, is prepared from ethyl iodide, C_2H_5I, just as methane is prepared from methyl iodide. It is also formed when methyl iodide is heated with zinc in a sealed tube, $2CH_3I + Zn = ZnI_2 + CH_3{\cdot}CH_3$; hence, ethane has been termed *dimethyl*.

Ethane is evolved from the anode when a solution of potassium acetate, CH_3COOK, is electrolysed; this salt dissociates into the ions CH_3COO and K, the former of which breaks up into C_2H_6 and CO_2, whilst the latter reacts with the water to form KOH and H, which is evolved at the cathode: the KOH absorbs the CO_2, so that the ultimate result may be approximately represented by the equation $2CH_3COOK + 2H_2O = C_2H_6 + 2KHCO_3 + H_2$.

Ethane resembles methane in properties, but is more easily liquefied (46 atm.); it is about twice as soluble in alcohol as methane is.

Propane, or *propyl hydride*, C_3H_8, is prepared by the action of nascent hydrogen on propyl iodide, $C_3H_7I + H_2 = C_3H_8 + HI$. It is also formed when a mixture of ethyl iodide and methyl iodide is heated with zinc, $CH_3{\cdot}CH_2{\cdot}I + CH_3I + Zn = CH_3{\cdot}CH_2{\cdot}CH_3 + ZnI_2$, the reaction being of importance as confirming the constitution of propane (Fig. 249), for it shows that the hydrocarbon is formed by the combination of methyl with ethyl. Propane is a colourless gas which boils at -45° C.

It will have been noticed that precisely similar methods serve for the preparation of methane, ethane, and propane. This is illustrative of the fact that the members of an homologous series of carbon compounds can generally be prepared from the members of another homologous series by the same reaction; thus the series of alkyl iodides (CH_3I, C_2H_5I, C_3H_7I, &c.) yield the corresponding series of alkyl hydrides (hydrocarbons) by metalepsis with (nascent) hydrogen. For each series of carbon compounds, therefore, there is a number of *general methods of formation*.

It will be noted that the hydrocarbons which are of industrial importance are either natural products, like the paraffins, or are obtained, like benzene, as products of destructive distillation, a process the mechanism of which has not yet been explained. Acetylene alone is manufactured by a process which may be said to be well understood. For the purposes of chemical investigation, however, several methods are available for preparing hydrocarbons, and are more or less generally applicable, whatever the family to which the desired hydrocarbon may belong.

Nucleal synthesis or *nucleal condensation* is the most general of these methods. The term implies the creation of a new carbon nucleus, either by adding another carbon atom to an existing nucleus or by converting a single bond between two carbon atoms in the molecule into a double or treble bond (*intra-molecular condensation*). In the case of the paraffins, in which the carbon atoms are always singly linked, the process must consist in adding new carbon atoms to the nucleus, and for this purpose two substituted hydrocarbons are treated with an agent capable of removing the substituent from each, leaving the carbon atoms of the two nuclei to combine at the points thus exposed. The equation given above for the formation of propane from ethyl or methyl iodides illustrates the process; in general terms $—RI + IR' + Na_2 = 2NaI + R{\cdot}R'$, in which R and R′ may be the same or different alkyl nuclei. The halogen substitution-products and sodium or zinc as the halogen remover are best suited for the method (*Wurtz's reaction*).

A less general method is the removal of carbon as CO_2 from an organic acid by heating it with alkali, as in the preparation of methane by heating sodium acetate with caustic soda (p. 144). This method is of much importance in the paraffin series, and is expressed by the general equation $R{\cdot}COONa + NaOH = RH + NaO{\cdot}COONa$. In a sense

it is the converse of the first method, since it forms a new carbon nucleus by removing carbon from an existing one.

A similar removal of carbon dioxide from salts of organic acids may be effected by electrolysis (see ethane, p. 531), and this method is applicable to several classes of hydrocarbons. It generally involves a nucleal condensation.

Other methods for preparing paraffins are (1) treatment of alkyl halides with nascent hydrogen, $RCl + H_2 = RH + HCl$ (see methane), and (2) interaction of alkyl iodides with zinc alkyl compounds, $2RI + ZnR_2 = 2(R.R) + ZnI_2$ (see ethane).

Butane, C_4H_{10}, is made by treating ethyl iodide with zinc (not in excess) in a sealed tube at 150° C.; $2C_2H_5I + Zn = ZnI_2 + C_4H_{10}$. It is much more easily condensed to a liquid than is either of the preceding hydrocarbons, and is much more soluble in alcohol. Liquid butane (sp. gr. 0.6) boils at 1° C. Since butane is prepared from ethyl iodide, it may be regarded as *diethyl* in the same sense that ethane is dimethyl, and it is justifiable to write its formula, $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$, or as in Fig. 252.

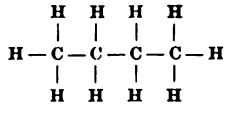


Fig. 252.—Normal butane.

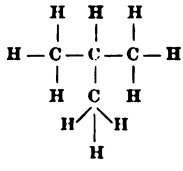


Fig. 253.—Secondary butane.

For ethyl iodide is the iodine substitution product of ethane, $CH_3{\cdot}CH_3$, and its formula is $CH_3{\cdot}CH_2I$. When the diad zinc acts upon this, it must take the I_2, which it requires to form zinc iodide, from two molecules of ethyl iodide, leaving the residues to combine and produce butane, thus:

$$CH_3{\cdot}CH_2I + Zn + ICH_2{\cdot}CH_3 = ZnI_2 + CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3.$$

There is a second hydrocarbon of the formula C_4H_{10}; it is prepared by the action of nascent hydrogen on a compound called *tertiary butyl iodide* (*q.v.*), C_4H_9I. It might be mistaken for butane but for the fact that it will not liquefy until cooled to −17° C. This second butane has been called *secondary butane* or *isobutane* (*ἴσος*, *equal*), the first butane being termed *normal butane*, from *norma*, a *rule*, because it is the product of the usual general methods of formation of the paraffins, and possesses the physical properties which the hydrocarbon, C_4H_{10}, should possess from its position in the homologous series of paraffins (*e.g.*, a boiling-point about 30° lower than the next higher member in the series). In order to explain the existence of this secondary butane it is supposed that the four carbon atoms are arranged in space differently from the manner in which they are arranged in the case of normal butane. A little consideration will show that the only possible second method of arrangement of the carbon atoms on one plane is that shown in Fig. 253, in which the fourth C atom is attached to the central C atom of the propane formula. The same arrangement may be expressed by the formula $CH_3{\cdot}C(CH_3)H{\cdot}CH_3$ or $(CH_3)_2{:}CH{\cdot}CH_3$, and may be de-

scribed as consisting of methane in which three atoms of H have been exchanged for methyl, that is as *trimethylmethane*. Tertiary butyl iodide has the formula $CH_3{\cdot}C(CH_3)I{\cdot}CH_3$, and the action of nascent hydrogen in converting it into trimethylmethane, or secondary butane, is apparent.

Pentane, C_5H_{12}. Three hydrocarbons of this formula exist; that which is made by the general methods, and, therefore, has a right to the title *normal pentane*, is a colourless liquid, boiling at 36° C. *Secondary pentane*, or *isopentane*, boils at 28° C., and *tertiary pentane* or *tetramethylmethane*, at 9° C. To account for the existence of these three hydrocarbons, it is necessary to suppose that the five carbon atoms are arranged in three different ways; this will be found to be possible, the results being indicated in Figs. 254–256, or by the formulæ $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$, $CH_3{\cdot}CH_2{\cdot}C(CH_3)H{\cdot}CH_3$, and $C(CH_3)_4$.

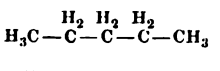


Fig. 254.—Normal pentane.

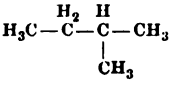


Fig. 255.—Iso-pentane.

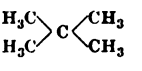


Fig. 256.—Tertiary pentane.*

If it were possible to arrange the 5 carbon atoms in a way essentially different from any of these three, a fourth pentane might be expected to exist. It will be evident that the greater the number of carbon atoms in the hydrocarbon, the greater the variety of arrangement and therefore the greater the number of possible *isomerides*. Thus, there may be discovered 802 compounds of the formula $C_{13}H_{28}$.

Isomerides are those compounds which have the same percentage composition and the same molecular weight, but different properties. Cases of *isomerism* are very numerous among the carbon compounds; attempts have been made to explain them by reference to the arrangement of the atoms of the compounds in space, although in some cases special difficulty is experienced; these will be referred to in due course.

Polymerides have the same percentage composition, but different molecular weights; *e.g.*, C_2H_2 and C_6H_6; CH_2O and $C_6H_{12}O_6$.

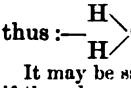
Since the valency of carbon is always four, there can only be three modes in which the carbon atoms can be linked to each other, giving rise to three main classes of isomerides, which are illustrated by the three classes of paraffin hydrocarbons. *Normal paraffins* are those in which all the carbon atoms are united in a single chain without branches, so that the formula begins and ends with CH_3, every other link being CH_2 (Fig. 254). *Secondary paraffins* or *iso-paraffins*, have at least one branch, that is, at least one carbon atom is united with three other carbon atoms, as in Fig. 255. *Tertiary paraffins* or *neo-paraffins*, have at least one carbon atom united to four others, as in Fig. 256.

The remaining hydrocarbons of the paraffin series do not need detailed consideration here. Those from hexane to *pentadecane* ($C_{15}H_{32}$) are colourless liquids the boiling-points of which increase, in the normal series, by about 30° C. for each increment of CH_2. Those in the normal series, from hexadecane ($C_{16}H_{34}$) to *pentatriacontane* ($C_{35}H_{72}$), the highest

* That this is really the constitution of neo-pentane is shown by the steps for obtaining it synthetically; acetone, $H_3C(CO)CH_3$, treated with PCl_5, yields $H_3C(CCl_2)CH_3$, and this acted on by zinc methyl, gives $H_3C[C(CH_3)_2]CH_3$, or neo-pentane.

known member, are colourless solids of which the melting-point increases by 3–4° C. for each increment of CH_2, that of hexadecane being 19° C.

Unsaturated Hydrocarbons.

317. All hydrocarbons which do not correspond with the general formula C_nH_{2n+2} are found to be capable of combining directly with the halogens without exchanging hydrogen for them. Such are, therefore, termed unsaturated hydrocarbons. No hydrocarbon has yet been discovered which contains an uneven number of hydrogen atoms, nor has any unsaturated hydrocarbon containing only one atom of carbon ever been isolated. To account for these facts it is supposed that all unsaturated hydrocarbons contain two or more carbon atoms which are united to each other by two or three atom-fixing powers, thus :—  , and H – C≡C – H.

It may be said that, in a hydrocarbon, *an unsaturated carbon atom cannot exist*; if there be not a sufficiency of other elements to saturate the carbon atom, it will combine by all its available atom-fixing powers with another carbon atom. The fact that no such hydrocarbon as $H_3C-\overset{|}{C}H_2$ is known, is in support of this statement. Of these two carbon atoms the unsaturated one will take up an atom-fixing power of the saturated carbon atom, at the expense of one of the hydrogen atoms united to this latter, forming $H_2C=CH_2$, in which neither carbon atom can be said to be unsaturated, although the compound *as a whole* is unsaturated. Treatment of this compound with chlorine will open up the double linking, yielding $H_2C(Cl)-CH_2(Cl)$. If the compound were represented by the formula $H_2C-\overset{|}{C}H_2$, there would be no apparent reason why, when the compound is mixed with the proper proportion of chlorine, one carbon atom alone should not combine with Cl yielding $H_2C(Cl)-CH_2$, a result which, however, has never been obtained. The same objection applies to a third possible method of representing this hydrocarbon, viz. : $H_3C-\overset{|}{C}H$; moreover, if this formula were correct the addition of chlorine to the hydrocarbon might be expected to produce $H_3C-CH(Cl)_2$, whereas there is evidence that the two chlorine atoms in the compound formed by addition of chlorine to C_2H_4 are attached to different carbon atoms.

A similar line of reasoning serves for supporting the formula HC≡CH for the hydrocarbon C_2H_2.

If two regular tetrahedra be placed with one edge of each coincident, there will be two solid angles of each tetrahedron left unattached. Such an arrangement may be supposed to represent the structure of the hydrocarbon C_2H_4 in space ; each carbon atom would occupy the centre of a tetrahedron, and each hydrogen atom would be attached to a free solid angle. By placing the two tetrahedra with one face of each coincident, the structure of the hydrocarbon C_2H_2 may be represented.

The following figures (Fig. 257) may represent hydrocarbons containing singly-linked, doubly-linked, and trebly-linked carbon atoms respectively.

Olefine Series of Hydrocarbons.—The *Olefine hydrocarbons* are unsaturated hydrocarbons containing a pair of doubly-linked carbon atoms ; they correspond in composition with the general formula C_nH_{2n}. The first three members of the homologous series are *ethylene*, $H_2C:CH_2$; *propylene*, $H_2C:CH\cdot CH_3$; and *butylene*, $H_2C:CH\cdot CH_2\cdot CH_3$. It will be seen that the nomenclature adopted differs from that for the paraffins by the substitution of the suffix *-ylene* for *-ane*, an alternative name for the olefines being *alkylenes*.

The olefines are found in petroleum-oil and in the products of the destructive distillation of coal, wood, &c. The first three members of the series are gaseous under ordinary conditions; the majority of the remainder are colourless liquids, but the highest members are solid. A gradation of boiling-points and melting-points is observed, similar to that existing in the paraffin series. The properties of ethylene may be considered as typical of those of the other members of this group of hydrocarbons.

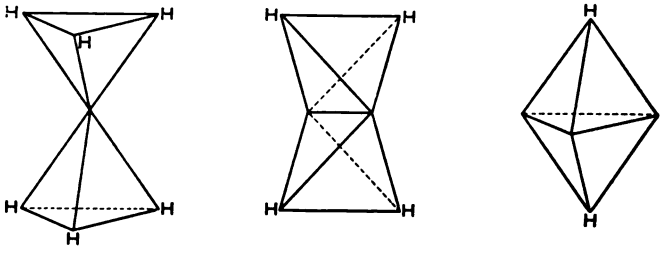


Fig. 257.

Olefiant gas, *ethylene*, or *ethene*, C_2H_4, is obtained by the action of powerful dehydrating agents on alcohol; $C_2H_5{\cdot}OH = C_2H_4 + HOH$. It may be prepared, as described at p. 142, by heating alcohol with twice its volume of strong sulphuric acid; secondary changes cause a carbonisation of the mixture, and the ethene is accompanied by some ether vapour, and by CO_2 and SO_2; the ether may be removed by passing the gas through strong sulphuric acid, and the dioxides by potash or soda.

It is also obtained by heating an ethyl halide with a caustic alkali in alcohol, *e.g.*, $C_2H_5Br + KOH = C_2H_4 + KBr + HOH$.

Properties of ethylene.—It has a faint ethereal odour, sp. gr. 0.97, and boils at -103° C. Slightly soluble in water; more soluble in alcohol. Burns with a bright luminous flame, which renders it very useful as an illuminating constituent of coal-gas. When mixed with chlorine, ethylene combines with it to form a fragrant liquid known as *ethylene chloride* or *Dutch liquid*, $ClH_2C{\cdot}CH_2Cl$. Bromine forms a similar compound with it. Sulphuric acid slowly absorbs ethylene, forming $C_2H_5HSO_4$, *sulphethylic* or *sulphovinic acid* or *ethyl hydrogen sulphate*, from which alcohol may be obtained by distillation with much water, and ethene by heating it alone, $C_2H_5HSO_4 + HOH = C_2H_5OH + H_2SO_4$, $C_2H_5HSO_4 = C_2H_4 + H_2SO_4$. Sulphuric anhydride absorbs ethene much more easily, and a strong solution of SO_3 in H_2SO_4 (fuming sulphuric acid) is employed for absorbing it in the analysis of coal-gas. The compound formed by SO_3 with ethylene is crystalline, and is termed *carbyl sulphate* or *ethionic anhydride*, $C_2H_4(SO_3)_2$. In contact with water, this forms *ethionic acid*, $CH_2(OSO_3H){\cdot}CH_2(SO_3H)$, and when this is boiled with water it yields *isethionic acid*, $H_2C_2H_4S_2O_7 + H_2O = H_2SO_4 + CH_2(OH){\cdot}CH_2(SO_3H)$. It will be noticed that isethionic acid has the same composition as ethyl hydrogen sulphate, but it is a more stable compound.

In presence of platinum-black, ethylene combines with hydrogen to

form ethane, C_2H_6. With HBr and HI it combines to form ethy-bromide, C_2H_5Br, and iodide, C_2H_5I, respectively.

Oxidising-agents, such as nitric and chromic acids, convert ethene into oxidised bodies containing two carbon atoms, such as oxalic acid, $C_2H_2O_4$, aldehyde, C_2H_4O, and acetic acid, $C_2H_4O_2$.

From the above description of the properties of ethene, it will be seen that it differs greatly from methane and the other paraffins, in the readiness with which it combines with other bodies, especially with chlorine, bromine, and sulphuric anhydride, forming *addition*-products instead of substitution-products.

Experiments which may be performed with the gas will be found at p. 143.

Propylene, C_3H_6 or $CH_3{\cdot}CH{:}CH_2$, occurs in small quantity in coal-gas. It may be obtained by heating glycerine with zinc-dust:

$$C_3H_5(OH)_3 + Zn_3 = C_3H_6 + H + 3ZnO.$$

In properties it resembles ethylene, but it is, of course, half as heavy again. It is more easily absorbed by strong sulphuric acid. Only one propylene is known, but another hydrocarbon, trimethylene, has the same formula (p. 539).

Butylene, C_4H_8 or $CH_3{\cdot}CH_2{\cdot}CH{:}CH_2$, occurs largely in the illuminating gas made by distilling the vegetable and animal oils. It is also found in the odorous hydrocarbons which are evolved when cast iron is dissolved in hydrochloric or dilute sulphuric acid. It boils at $-5°$ C.

Consideration of the formula for butylene will show that three isomerides of this hydrocarbon can exist, viz., α- or *normal butylene*, $CH_3{\cdot}CH_2{\cdot}CH{:}CH_2$; β- or *pseudo-butylene*, $CH_3{\cdot}CH{:}CH{\cdot}CH_3$; and γ- or *iso-butylene* $(CH_3)_2C{:}CH_2$. The butylene described above is the normal hydrocarbon. Pseudo-butylene exists in two modifications called geometrical isomerides (see p. 542).

Amylene or *pentylene*, C_5H_{10} or $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CH_2$, can exist in five isomeric forms. They occur in petroleum and paraffin oil. The normal amylene, which has the formula given above, boils at 40° C.

The moderate oxidation of the olefines, in presence of water, produces compounds in which the opened up bonds are attached to hydroxyl groups; thus, $CH_3{\cdot}CH{:}CH_2$ yields $CH_3{\cdot}CHOH{\cdot}CH_2OH$.

General methods for preparing olefine hydrocarbons.—(1) It is obvious that if one of the single bonds in a paraffin be converted into a double bond the corresponding olefine will be produced, *e.g.*, propane, $CH_3{\cdot}CH_2{\cdot}CH_3$, will become propylene, $CH_3{\cdot}CH{:}CH_2$. This is a nucleal condensation, and may be effected similarly to that by which new paraffins may be formed (p. 531). Thus, a dihalogen substituted paraffin may be heated with zinc, $CH_2Br{\cdot}CH_2Br + Zn = CH_2{:}CH_2 = ZnBr_2$. For this kind of condensation, however, heating a monohalogen derivative with an alcoholic solution of an alkali is generally best; in this case the halogen atom and a hydrogen atom are removed, presumably as hydrogen halide, by the alkali; $CH_3{\cdot}CH_2Br = CH_2{:}CH_2 + HBr$.

(2) By the dehydration of the alcohols of the paraffin series (*q.v.*) by strong sulphuric acid, zinc chloride, or phosphoric acid, *e.g.*, $CH_3{\cdot}CH_2{\cdot}CH_2OH = CH_3{\cdot}CH{:}CH_2 + HOH$.

The second method frequently produces a mixture of the olefine and its *polymerides* (p. 533), for the olefines tend to polymerise under the influence of acids and dehydrating agents; thus, when amylene is prepared in this way, $C_{10}H_{20}$ and $C_{15}H_{30}$ are also produced.

(3) The salts of some of the dicarboxylic acids (*q.v.*) yield olefines when electrolysed (*cf.* p. 531); thus potassium succinate yields ethylene:

$$CO_2K{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2K + 2HOH = CH_2{:}CH_2 + 2KHCO_3 + H_2.$$

(4) The process of nucleal condensation may be reversed; that is to say, a treble or double linking may be converted into a single linking by treating the

compound with nascent hydrogen. Thus some of the acetylene compounds yield the corresponding olefine when so treated: $CH \vdots CH + H_2 = CH_2 : CH_2$ (similarly, ethylene may be transformed into ethane—see above).

(5) Wurtz's reaction (p. 531) may be applied to produce new olefines by treating a mixture of a monohalogen-substituted olefine and an alkyl halide with sodium.

318. **Acetylene Series of Hydrocarbons.**—The *acetylene hydrocarbons* are unsaturated hydrocarbons containing a pair of trebly-linked carbon atoms: they correspond in composition with the general formula C_nH_{2n-2}. The first two members of the series, *acetylene*, $HC \vdots CH$, and *allylene*, $H_3C{\cdot}C \vdots CH$, are gaseous under ordinary conditions, whilst most of the others are colourless liquids.

It will be seen that the hydrocarbon, C_3H_4, is capable of being represented by the two formulæ $CH_3{\cdot}C \vdots CH$, and $CH_2 : C : CH_2$, so that two modifications of this compound may be expected: these have been prepared, the former being called *allylene* and the latter *allene* or *propadiene*.* For every true acetylene (a hydrocarbon containing a pair of trebly-linked carbon atoms) there may also be a hydrocarbon containing two pairs of doubly-linked carbon atoms. These *dioleſines* differ considerably in properties from the acetylenes; they are unimportant, and cannot be further considered here.

Acetylene, or *ethine*, C_2H_2, is the only hydrocarbon which can be formed in more than mere traces by the direct union of its elements. Its preparation and most of its properties have been described at p. 137.

Pure acetylene may be prepared from ethylene by combining this with bromine to form ethylene bromide which is then heated with caustic potash in alcohol:

$$BrH_2C{\cdot}CH_2Br + 2KOH = HC \vdots CH + 2KBr + 2HOH;$$

and from methane by converting this into chloroform which is then heated with sodium:

$$HC \vdots Cl_3 + Cl_3 \vdots CH + Na_6 = HC \vdots CH + 6NaCl;$$

These two reactions are typical of the *general methods for preparing acetylene*.

In the presence of platinum-black acetylene combines with hydrogen to form ethene, C_2H_4. Strong sulphuric acid absorbs acetylene slowly as it does ethene; but when the solution is mixed with water and distilled, it yields, not alcohol as with ethene, but *croton-aldehyd*, $C_3H_5{\cdot}CHO$; $2C_2H_2 + H_2O = C_4H_6O$. Chromic acid oxidises acetylene to acetic acid; $C_2H_2 + H_2O + O = C_2H_4O_2$. Alkaline potassium permanganate converts it into oxalic acid, $C_2H_2 + O_4 = C_2H_2O_4$.

The most remarkable feature of acetylene is the facility with which its hydrogen is displaced by metals. By heating sodium in acetylene, C_2HNa, *mono-sodium acetylide* and C_2Na_2, *disodium acetylide* may be obtained. *Cuprous acetylide*, C_2Cu_2 has been noticed at p. 140.

Silver acetylide, C_2Ag_2, is produced as a white precipitate when acetylene is passed into ammoniacal silver nitrate; in absence of ammonia the precipitate is a compound of the acetylide with silver nitrate.

When acetylene is passed into antimonic chloride, kept cool, crystals

* According to one system of nomenclature the terminations *-diene*, *-triene*, *-tetrene*, &c., are used to indicate hydrocarbons containing 2, 3, 4, &c., double linkings respectively. The position of the double bonds are indicated by the numbers of the C atoms immediately preceding them in the chain. Thus 1 : 4 -hexadiene is $CH_2 : CH \cdot CH_2 \cdot CH : CH \cdot CH_3$. Similarly, hydrocarbons containing 2, 3, 4, &c., treble bonds terminate in *-diine*, *-triine*, *-tetrine*, &c. respectively.

of $C_2H_2Cl_2{\cdot}SbCl_3$ are formed, which, on heating, yield the *acetylene dichloride*, $C_2H_2Cl_2$, as a liquid smelling like chloroform, and boiling at 55° C. $C_2H_2Cl_4$, *acetylene tetrachloride* and C_2HCl, *monochloracetylene*, have also been obtained.

When heated in a sealed tube, acetylene is partially converted into a mixture of two liquids, *benzene*, C_6H_6 and *styrolene*, C_8H_8. By passing electric sparks through a mixture of acetylene with nitrogen, *hydrocyanic acid* is produced; $C_2H_2 + N_2 = 2HCN$. Hence this acid, from which a large number of organic bodies may be derived, has been synthetised from its elementary constituents. Cuprous acetylide, in contact with zinc and solution of ammonia, yields ethylene, which is convertible into alcohol, and from this a very large number of organic compounds may be made.

Acetylene is regarded as one of the most important intermediate bodies in the synthesis of organic compounds from their elements.

Allylene, or *propine*, $CH_3{\cdot}C \vdots CH$, resembles acetylene, but its cuprous compound is yellow instead of red.

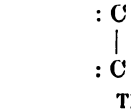
The hydrocarbon C_4H_6 (*butine*) can exist in two forms, each of which will have a pair of trebly-linked carbon atoms, namely, $CH_3{\cdot}CH_2{\cdot}C \vdots CH$ (*ethylacetylene*) and $CH_3{\cdot}C \vdots C{\cdot}CH_3$ (*crotonylene* or *dimethylacetylene*); besides these true acetylenes, there is *diallyl*, $CH_2 : CH{\cdot}CH : CH_2$, a diolefine found in compressed illuminating gas.

Crotonylene is a liquid (b.-p. 27° C.); its vapour is one of the illuminating hydrocarbons in coal-gas. It does not form any metallic derivatives, and it appears that this is generally the case with those acetylenes which have not the group $\cdot C \vdots CH$ in their composition.

The other members of the series have no practical importance at present. They are prepared by treating the bromo-substitution products of the paraffins and olefines with alcoholic potash.

319. The paraffins, olefines, and acetylenes are supposed to have their carbon atoms linked together in what may be termed an *open chain*, in which there are terminal carbon atoms, each attached to only one other carbon atom. The hydrocarbons next to be considered, notably benzene and its homologues, exhibit properties which show that while they are strictly unsaturated in the sense that they do not correspond with the general formula C_nH_{2n+2} (p. 527), they behave more like the paraffins than the olefines towards chemical agents. The most fruitful hypothesis in explanation of this difference is that in these hydrocarbons no carbon atom is attached to only one other carbon atom. This can only be the case if the terminal carbon atoms are attached to each other, thus :—

Such hydrocarbons are termed *closed-chain* hydrocarbons, or *ring* or *cyclic* hydrocarbons—since the arrangement of the carbon atoms in the form of a ring is somewhat more convenient, *e.g.*,



The only other series of open-chain hydrocarbons which are known besides the three already considered are those corresponding with the general formulæ C_nH_{2n-4} and C_nH_{2n-6}. The hydrocarbons of the former series must have either one pair of trebly- and one pair of doubly-linked carbon atoms, as in the formula $CH_3{\cdot}CH : CH{\cdot}C \vdots CH$ (*olefine-acetylenes*), or three pairs of doubly-linked carbon atoms, as in $CH_2{\cdot}CH : C : C : CH_2$ (*triolefines*). The C_nH_{2n-6} open-chain hydrocarbons must contain either two trebly-linked or four doubly-linked carbon atoms;

the treble linking is the more common, *e.g.*, *di-acetylene*, CH ⋮ C·C ⋮ CH, and *dipropargyl* (*hexadiine*), CH ⋮ C·CH_2·CH_2·C ⋮ CH, which is isomeric with benzene. Both these hydrocarbons form copper and silver compounds like those of acetylene.

Closed-chain Hydrocarbons.—It is obvious that a closed-chain hydrocarbon must contain at least three carbon atoms, and that such a one would be obtained if a hydrogen atom could be removed from each end of the propane chain, leaving the carbon bonds thus liberated to unite: $H_3C \cdot CH_2 \cdot CH_3 - H_2 = H_2C \cdot CH_2 \cdot CH_2$. This has not been accomplished directly, but if a bromine atom is substituted for a hydrogen atom in each CH_3 group, producing trimethylene bromide, $BrH_2C \cdot CH_2 \cdot CH_2Br$, these bromine atoms can be removed by sodium, whereupon the gas *trimethylene* * or *cyclopropane* is formed by *nucleal condensation* (*cf.* p. 531). Several *polymethylenes* or *cycloparaffins* of this type have been prepared in an analogous manner. *Pentamethylene* or *cyclopentane*, $CH_2\langle^{CH_2 \cdot CH_2}_{CH_2 \cdot CH_2}$, is important as a near relative of camphor, while *hexamethylene* or *cyclohexane* is transitional between the paraffins and benzene. All these hydrocarbons are isomeric with the olefines, from which they differ in not being attacked by permanganate; this is presumed to be conclusive that they do not contain double linking, and allies them to the saturated hydrocarbons.

Tetramethylene has not been prepared, but *methyltetramethylene* is known. Penta- and hexamethylene (naphthene) are found in Caucasian petroleum; the former boils at 50° C. *Heptamethylene* boils at 117° C. and is related to the acid found in cork (suberic acid).

When the iodo-substitution products of these hydrocarbons are treated with potash, the iodine is removed as HI, and a double linking is introduced; for instance, $CH_2\langle^{CHI \cdot CH_2}_{CH_2 - CH_2}$ yields $CH\langle^{CH \cdot CH_2}_{CH_2 \cdot CH_2}$, *cyclopentene*, which may be termed a *cyclo-olefine*. By repeating the operation, *cyclopentadiene*, $CH\langle^{CH:CH}_{CH:CH}$, is obtained; this is a *cyclodiolefine* found in crude benzene and boils at 41° C. It is easily attacked and yields addition-products, indicative that it contains double linking. If the closed chain contains three double bonds it is called a *cyclotriolefine*; thus benzene is *cyclohexatriene*.

There are several methods of producing nucleal condensation, besides that here given, for obtaining polymethylene derivatives; some of these will receive notice in the proper place.

Benzene Series of Hydrocarbons.—The general formula for this series is C_nH_{2n-6} where n is any whole number not smaller than 6. The series was originally called the *aromatic series* because the first hydrocarbons discovered were obtained from aromatic balsams and resins. Benzene itself is C_6H_6, and its homologues are formed from it by exchanging hydrogen for CH_3; thus, toluene, $C_6H_5CH_3$; xylene $C_6H_4(CH_3)_2$; &c. Before the structure of these hydrocarbons is considered some of their properties must be described.

320. **Benzene,** C_6H_6, occurs abundantly in the *light oil* obtained in the distillation of coal-tar. It is also found in petroleum. From the light oil it is obtained by fractional distillation; the portion which distils between 79° and 82° C. consists chiefly of benzene, and is purified by cooling it below 0° C. when the benzene crystallises, while the other

* The group CH_2 is termed methylene.

hydrocarbons remain liquid and are removed by pressure. A characteristic impurity of commercial benzene is thiophen, C_4H_4S (*q.v.*).

Benzene is an ethereal liquid, having the odour of coal-gas, of which its vapour is one of the illuminating constituents. Sp. gr. 0.88; m.-p. 5·5° C.; b.-p. 80° C. It is very inflammable, and burns with a red smoky flame; but its vapour, when mixed with air or hydrogen (as in coal-gas), burns with a bright white flame. Benzene is nearly insoluble in water, but dissolves in alcohol and ether. It is chiefly used for conversion into aniline (*q.v.*), but also for dissolving fats, caoutchouc, &c. If benzene be dropped into the strongest nitric acid, or into a mixture of ordinary concentrated nitric acid with an equal volume of strong sulphuric acid, a violent action occurs, red fumes are evolved, and the liquid becomes red. On pouring it into several times its volume of water, a heavy, oily liquid falls which is *nitrobenzene*, $C_6H_5NO_2$; $C_6H_6 + NO_2{\cdot}OH = C_6H_5NO_2 + HOH$.

The red fumes are the result of a secondary reaction not expressed in the equation. The sulphuric acid is used to combine with the water, since weak nitric acid does not act on benzene. Nitrobenzene has a powerful odour of almonds, and is sold, dissolved in alcohol, as *Mirbane essence*, for use in confectionery and perfumery. It is, however, a poisonous substance in large doses. It is also largely employed for the preparation of aniline. Nitrobenzene boils at 209° C.; its sp. gr. at 0° C. is 1.2; m.-p. 3° C.

If the mixture of nitric and sulphuric acids be boiled with the benzene, the liquid deposits on cooling, a yellowish crystalline solid which is *dinitrobenzene*, $C_6H_4(NO_2)_2$, a compound used in some explosives;

$$C_6H_6 + 2(NO_2{\cdot}OH) = C_6H_4(NO_2)_2 + 2HOH$$

Strong sulphuric acid also oxidises part of the hydrogen in benzene, when heated with it, leaving in its place the *sulphonic group*, or *sulphonic acid residue*, $SO_2{\cdot}OH$, which bears the same relation to sulphuric acid, $SO_2(OH)_2$, as nitroxyl, NO_2, bears to nitric acid, $NO_2{\cdot}OH$; thus, $C_6H_6 + SO_2(OH)_2 = HOH + C_6H_5{\cdot}SO_2{\cdot}OH$ (*benzene-sulphonic acid*). If fuming sulphuric acid be used, a second atom of hydrogen may be exchanged, forming *benzene-disulphonic acid*, $C_6H_4(SO_2{\cdot}OH)_2$.

When chlorine is passed into benzene (containing a little iodine, which assists the reaction), *monochlorobenzene*, C_6H_5Cl, is formed; it is an almond-smelling liquid, which boils at 132° C., is not decomposed by caustic alkalies, and is reconverted into benzene by water and sodium-amalgam (to yield nascent hydrogen). The further action of chlorine on benzene yields

Dichlorobenzene, $C_6H_4Cl_2$	Tetrachlorobenzene, $C_6H_2Cl_4$
Trichlorobenzene, $C_6H_3Cl_3$	Pentachlorobenzene, C_6HCl_5

Hexachlorobenzene, C_6Cl_6

These are all crystalline solid bodies.

Besides these *substitution-products*, benzene is capable of forming *addition-products* with chlorine; *benzene dichloride*, $C_6H_6Cl_2$; *tetrachloride*, $C_6H_6Cl_4$; *hexachloride*, $C_6H_6Cl_6$. These are less stable than the substitution-products; thus, the hexachloride, when heated with potash dissolved in alcohol, yields trichlorobenzene;

$$C_6H_6Cl_6 + 3KOH = C_6H_3Cl_3 + 3KCl + 3H_2O.$$

When benzene is treated with hydrogen dioxide, it is slowly converted into *hydroxybenzene* or *phenol*; $C_6H_6 + H_2O_2 = C_6H_5{\cdot}OH + H_2O$.

Benzene was so called because it was first prepared by distilling benzoic acid with slaked lime (3 parts); $C_6H_5{\cdot}CO_2H + Ca(OH)_2 = C_6H_6 + CaCO_3 + H_2O$. This method is still adopted for preparing perfectly pure benzene.

Benzene is detected by first converting it into nitro-benzene and reducing this to aniline (*q.v.*), which is recognised by its reaction with bleaching-powder.

321. *Constitution of benzene.*—A saturated hydrocarbon is one which corresponds with the general formula C_nH_{2n+2}, so that it is evident that benzene is an unsaturated hydrocarbon. It has been seen that the unsaturated hydrocarbons already considered (ethylene, acetylene, &c.) are so termed because of their capability of uniting directly with chlorine or bromine, and it has been noticed that the molecule of a hydrocarbon will combine with 2, 4, &c., atoms of Cl or Br according to its degree of unsaturation, so that the final product of such combination is always a compound of the general type, $C_nH_{2n-x}X_{x+2}$, where X is Cl or Br. This compound is a stable one and does not combine with any more halogen. Moreover, this reaction between the unsaturated hydrocarbon and the halogen is the primary reaction between the two substances.

The reaction between benzene and a halogen is of a different nature from this. As has been stated above, it is more easy to obtain halogen-substitution-products—*i.e.*, those in which halogen is substituted for hydrogen—from benzene, than it is to obtain mere addition-products, containing halogen added to the hydrocarbon. This recalls the behaviour of paraffin hydrocarbons.

It seems, then, that benzene resembles both the saturated and unsaturated hydrocarbons in its behaviour towards halogens. It differs, however, from the former class in that it can form addition-products with the halogens, and from the latter (*e.g.*, its isomeride dipropargyl) in that the most saturated derivative obtainable from it corresponds with the general formula $C_nX'_{2n}$ and not with C_nX_{2n+2}. When benzene is heated with excess of hydriodic acid it is converted into the hydrocarbon C_6H_{12}, thus: $C_6H_6 + 6HI = C_6H_{12} + I_6$. This *benzene hexahydride* (cyclohexane) is isomeric with the olefine hexylene, which, however, might be expected to become hexane, C_6H_{14}, when heated with excess of hydriodic acid.

These facts with regard to benzene may easily be explained on the hypothesis that the six carbon atoms form a closed chain (p. 538). It will be seen at once that all closed-chain compounds must contain a carbon nucleus which is possessed of two fewer atom-fixing powers than the corresponding carbon nucleus in an open-chain compound has; for instance, the nucleus ·C·C·C·C·C·C· has 14 atom-fixing powers, whilst the nucleus ·C·C·C·C·C·C· has only 12 atom-fixing powers.

The closed-chain formula for benzene must contain three pairs of doubly-linked carbon atoms, if all the affinities of each atom are to be represented as satisfied in the same way as they are represented in open-chain compounds. Since, as will be shown, there is reason to believe that the structure of the benzene molecule in space is symmetrical, it is

customary to represent these three double bonds symmetrically in the formula, which is therefore written in the form shown in Fig. 258, and known as *Kekulé's benzene ring*.

Some support is lent to this formula by the fact that acetylene polymerises into benzene when it is heated. HC ⋮ CH + HC ⋮ CH + HC ⋮ CH becoming HC:CH·HC:CH·HC:CH ; and that allylene CH ⋮ C·CH_3 is polymerised by strong H_2SO_4 to 1 : 3 : 5 -*trimethylbenzene* or *mesitylene* (*q.v.*). There are, however, some grave objections to Kekulé's formula which will be noticed in the sequel.

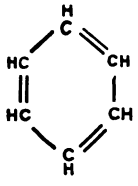


Fig. 258.

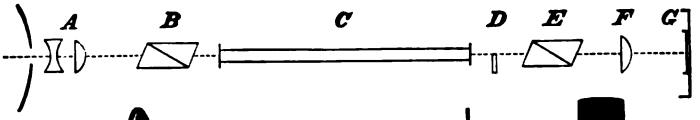
322. *Position-isomerism.* — Isomerides have already been defined as compounds which have the same percentage composition and the same molecular weight, but different properties. The isomerism may be due to one of three causes. (1) The isomeric compounds may be composed of different radicles, thus, the compounds C_2H_5·CO·C_2H_5 and CH_3·CO·C_3H_7 are isomeric; such isomerides are sometimes termed *metamerides*. (2) The isomeric compounds may consist of the same radicles, but these may be attached to different carbon atoms; an example was met with in the case of pentane (p. 533); such isomerides may be termed *position-isomerides*. (3) The isomeric compounds may have the same radicles, attached to the same carbon atoms but differently situated in space with regard to each other; such cases will be met with hereafter (lactic acids); these isomerides are termed *stereo-isomerides*, and in one class of this kind of isomerides the main difference between the members is in their action on polarised light, each existing in two *optically active* forms—namely, one which rotates the plane of polarisation of light to the right (*dextro-rotatory*) and another which rotates the plane equally to the left (*laevo-rotatory*)—and in two *optically inactive* forms.

An account of the polarisation of light must be sought in a work on Physics. It may be said here that when a ray of light is passed through a certain kind of crystal (a polariser) in a certain direction, it is broken into two rays pursuing different paths. Each of these rays is of such a nature (polarised) that while it will pass through a similar crystal (the analyser) placed with its axis parallel to that of the first, it is extinguished if the second crystal be rotated through an angle of 90°. If, while the axes of the crystals are in this relative position, a solution of a dextro-rotatory compound be placed between them, the ray will pass again through the analyser (a result expressed by saying that the plane of polarisation has been rotated) and this must be turned to the right through a certain angle before the light is again extinguished; the measure of this angle is a measure of the optical activity or *rotatory power* of the compound dissolved. A laevo-rotatory compound produces the same effect, but in the opposite direction.

The instrument whereby the rotatory power is ascertained is called the *polarimeter*, and is shown in Fig. 260. The essential parts of it are the prisms and lenses, the arrangement of which is represented in Fig. 259. The light from the lamp, shown in Fig. 260 (which burns with a non-luminous flame, made luminous by the introduction of a sodium compound, so that it yields light of one colour only), passes first through a plate *G* cut from a crystal of potassium bichromate to ensure monochromatism, then successively through a lens *F* to make the beam parallel, the Nicol polarising prism *E*, a quartz plate *D* covering one half of the field of vision, the tube *C*, with glass ends and containing the solution to be examined, the Nicol prism analyser *B*, and the opera-glass combination of lenses *A* focusing on to the plate *D*. According to the relative angular positions of *E* and *B*, the field viewed through *A* will be either of uniform shade or will have one-half darker than the other, this effect being due to the quartz plate *D*. In using the

instrument the tube *C* is inserted after the analyser has been rotated to produce the uniform shade; if the solution has rotatory power the field will no longer be of uniform shade, the one half or the other being the darker accordingly as the rotation is dextro- or laevo-. The analyser is then again rotated to produce the uniform tint, and the angle of rotation is read off on the circular scale through one of the eye pieces.

Fig. 259.—Parts of the polarimeter.



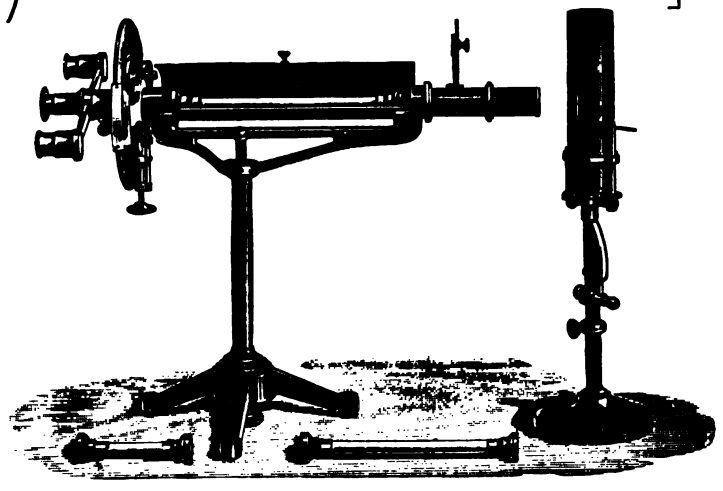


Fig. 260.—Polarimeter.

Position-isomerides which are mono-substitution derivatives* of a hydrocarbon have only been found to exist in those cases where the carbon atoms in the nucleus are not all similarly united to each other. Thus, two monobromethanes, C_2H_5Br, have never been prepared, and it is concluded that more than one cannot exist because, since there are only two carbon atoms in the nucleus, these must be similarly united to each other. There can, however, be two monobromopropanes C_3H_7Br, because the carbon nucleus contains three carbon atoms, one of which is united with two other carbon atoms and two hydrogen atoms, whilst the other two are, each of them, only united to one other carbon atom and to three hydrogen atoms; thus, the two compounds $H_3C{\cdot}CH_2{\cdot}CH_2Br$ (*normal propyl bromide*) and $H_3C{\cdot}CHBr{\cdot}CH_3$ (*isopropyl bromide*) may be expected to be different from each other, probably because the centre of gravity of the molecule of each is not the same, owing to the difference in the point of attachment of the bromine atom. That these two compounds exist there is no doubt, and that they have the formulæ above ascribed to them is rendered highly probable from the methods of their formation, which will be discussed anon.

* Substitution-derivatives are mono-, di-, tri-, &c., accordingly as the element or radicle is substituted for one, two, three, &c., hydrogen atoms.

From what has been said, it will be understood that the fact that only *one mono-substitution product of benzene* can be found to exist, no matter what the substituting element or radicle be, is strong support in favour of the similarity of linking between all the carbon atoms, and of the symmetrical structure of the molecule. Thus monobromobenzene, C_6H_5Br, can be produced in several ways, yet it always has precisely the same properties.

It can, of course, be objected that it may happen that by the various methods of preparing this compound the same H atom is always exchanged for Br, so that this element is always attached to the same carbon atom, and could it be attached to some other of the six atoms a different monobromobenzene would be produced. The following line of argument, involving reactions which will be understood later, refutes this objection. Monobromobenzene is prepared by the direct action of bromine on benzene, and may have been formed by the substitution of Br for any one of the six H atoms in the benzene ring (Fig. 258). Assume that H (1) has been substitued, so that the product may be represented as $C_6BrH\overset{2}{H}\overset{3}{H}\overset{4}{H}\overset{5}{H}\overset{6}{H}$. By treating this with HNO_3, the compound $C_6H_4Br(NO_2)$ is produced, and it is reasonable to admit that the second H atom, which has been exchanged for NO_2, is not the same H atom as that previously exchanged for Br. Assume that H (2) has been exchanged for NO_2, then the nitro-compound will be $C_6Br(NO_2)\overset{3}{H}\overset{4}{H}\overset{5}{H}\overset{6}{H}$. By treating this with nascent hydrogen (neglecting another reaction) the Br may be removed, and the H whose place it occupied reinstated, so that nitrobenzene of the formula $C_6\overset{1}{H}(NO_2)\overset{3}{H}\overset{4}{H}\overset{5}{H}\overset{6}{H}$ is produced. By treatment with reducing-agents this is converted into an amido-substitution-derivative $C_6\overset{1}{H}(NH_2)\overset{3}{H}\overset{4}{H}\overset{5}{H}\overset{6}{H}$. When this is treated, under certain conditions, with nitrous acids it yields the compound called diazobenzene, $C_6\overset{1}{H}(N_2)\overset{3}{H}\overset{4}{H}\overset{5}{H}\overset{6}{H}$, and by decomposing this with hydrobromic acid, monobromobenzene, $C_6\overset{1}{H}Br\overset{3}{H}\overset{4}{H}\overset{5}{H}\overset{6}{H}$ is obtained, and this is found to be identical with the bromobenzene produced directly from bromine and benzene, showing that whether H (1) or H (2) is exchanged for Br, the same substance is produced.

The cases of position-isomerism among poly-substitution derivatives of hydrocarbons are very numerous. Two dibromo-derivatives of ethane are known to exist, viz.: $CH_2Br{\cdot}CH_2Br$ and $CH_3{\cdot}CHBr_2$. It has been found that there are four *dibromopropanes*, $C_3H_6Br_2$, and from the methods of their formation there is reason to believe that they are represented by the formulæ, (1) $CH_2Br{\cdot}CH_2{\cdot}CH_2Br$, (2) $CH_3{\cdot}CHBr{\cdot}CH_2Br$, (3) $CH_3{\cdot}CH_2{\cdot}CHBr_2$, and (4) $CH_3{\cdot}CBr_2{\cdot}CH_3$. Only two other methods of writing this formula are possible, viz., (5) $CH_2Br{\cdot}CHBr{\cdot}CH_3$ and (6) $CHBr_2{\cdot}CH_2{\cdot}CH_3$; but in (5) the Br atoms are attached to carbon atoms, which are the same, so far as their linking to other atoms is concerned, as the carbon atoms to which the Br atoms are attached in (2), and there is the same similarity between (6) and (3). It is evident that if the number of carbon atoms in the open-chain hydrocarbon-nucleus, or the number of substituting bromine atoms, be increased, the number of forms in which the formula can be written so that this is essentially different each time, will be increased. It has been supposed that as many isomerides may exist as there are essential differences in the formulæ which can be written for the compound; whilst many isomerides, thus prophesied, have been prepared, the number remaining to be discovered is so large that some hesitancy may reasonably be shown in accepting the supposition.

In the case of benzene the poly-substitution-products have been very thoroughly examined. Most of the di-substitution-products are known in three isomeric forms, but no *di-substitution-product of benzene has been prepared in more than three isomeric forms.*

Thus, although benzene yields only one mono-substitution-product, it forms three *di-substitution*-products, in each of which two atoms of hydrogen have been exchanged for radicles or for other elements.

There are, then, three di-bromobenzenes, all having the formula $C_6H_4Br_2$, and therefore strictly isomeric, and yet having different properties; so there are three di-nitro-benzenes, $C_6H_4(NO_2)_2$, and three benzene di-sulphonic acids, $C_6H_4(SO_3H)_2$, and such compounds form perfectly distinct series, so that if they be distinguished as *a*, *b*, and *c* compounds, *a*-di-bromobenzene will yield *a*-di-nitrobenzene, and *a*-benzene-di-sulphonic acid, while *b*- and *c*-di-bromobenzenes will also yield their proper series of derivatives.

To explain the existence of these three isomeric di substitution-products, it is necessary to assume that different *pairs* of hydrogen atoms in benzene have different chemical values, and that the properties of the di-substitution-products depend upon the particular pair of hydrogen atoms exchanged. In order to investigate this it became necessary to *orient* (as it is termed in surveying) the plan of the benzene formula, that is, to mark the situation or *bearing* of its different parts.

To effect this *orientation of the benzene ring*, it is necessary to distinguish the carbon atoms, for which purpose they are numbered consecutively as on a watch-face (Fig. 261).

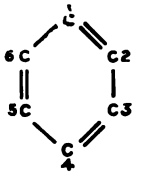


Fig. 261.

The pairs of hydrogen atoms occupying places 1 and 2, 2 and 3, 3 and 4, 4 and 5, 5 and 6, 6 and 1, bear the same relation to the figure, and are therefore of equal value, so that whichever pair is exchanged for other radicles, the same di-substitution-product will be obtained.

Again, 1 and 3, 2 and 4, 3 and 5, 4 and 6, 5 and 1, 6 and 2, being alternate atoms, bear the same relation to the figure, and their substitution would give rise to the same di-substitution-product.

But consecutive atoms, such as 1 and 2, or 2 and 3, have a different relation to the figure from that belonging to alternate atoms, such as 1 and 3, or 2 and 4, so that the substitution of two consecutive atoms of hydrogen would give one kind of derivative (say the *a*-substitution-product), and that of two alternate atoms would produce another kind (say the *b*-substitution-product).

Lastly, the pairs 1 and 4, 2 and 5, 3 and 6, have the same relation to the figure, and, when exchanged for other radicles, would give identical products, but these would be different from the *a* and *b* products, and may be called the *c*-substitution-products.

As the above lists exhaust all the possible pairs of hydrogen atoms, there can be only three di-substitution derivatives of benzene. Instead of using *a*, *b*, and *c* to distinguish the three isomerides, it is customary to use the prefixes *ortho-*, *meta-*, and *para-*, respectively. When *adjacent* hydrogen atoms in the benzene ring are exchanged for other radicles, the product is an *ortho*-compound; when *alternate* hydrogen atoms are substituted, the product is a *meta*-compound; when *opposite* hydrogen

atoms are substituted, the product is a *para*-compound. This is sometimes denoted by figures prefixed to the formula: thus 1 : 2-dibromobenzene is *ortho-dibromobenzene;* 1 : 3 is *meta-dibromobenzene;* and 1 : 4 is *para-dibromobenzene*, all having the formula $C_6H_4Br_2$.

This fact, that there are only three di-substitution-products of benzene, constitutes the main objection to Kekulé's formula. It is not in accord with experience obtained from the open-chain compounds, that a substitution-derivative containing the substituent groups attached to carbon atoms doubly linked together, should be identical with one which contains the groups attached to singly-linked carbon atoms: thus 1 : 2-dinitrobenzene should differ in properties from 1 : 6-dinitrobenzene, though as a fact these two compounds are identical, and four di-substitution-products are not known. Kekulé gets over this objection by supposing that the ring is in constant vibration, the double links and single links changing places every swing. Several other formulæ have been proposed, notably the so-called "diagonal formula" of Claus, the conception underlying which will be appreciated from Fig. 262.

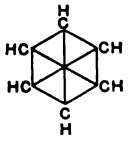


Fig. 262.

An argument in support of this formula is the high resistance shown by benzene and some of its substitution-products to direct oxidation (by alkaline permanganate, for example), thus indicating that "ethylenic linking"—*i.e.*, carbon doubly linked, as in ethylene —does not occur. On the other hand many addition products of benzene, in which all the carbon atom-fixing powers are not satisfied are so easily oxidised that ethylenic linking may be supposed to exist in them. Baeyer believes in the existence of ethylenic linking in some benzene compounds and of *central* or "*para-*" *linking* (much as in Fig. 262) in others.

Pending a better knowledge as to the disposition of the fourth atom-linking-power of each carbon atom, the majority of chemists prefer to represent benzene compounds as derived from a plain hexagon.

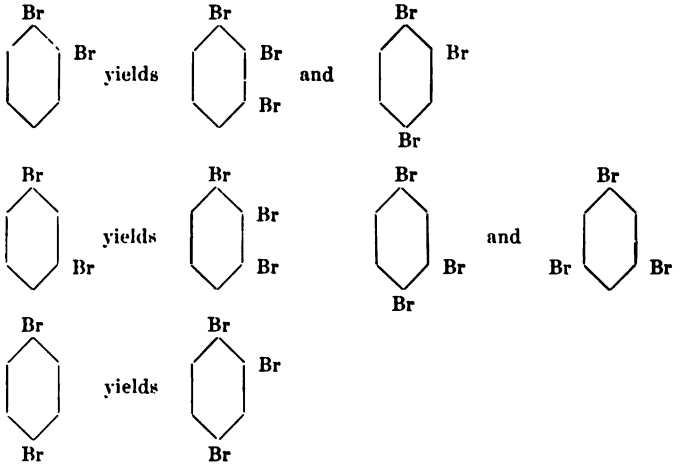
Tri-substitution derivatives of benzene, in which the same radicle is substituted for all three atoms of hydrogen, are found to exist in three isomeric forms; thus, there are three *tribromobenzenes*, $C_6H_3Br_3$, distinguished as *adjacent* (1 : 2 : 3), *symmetrical* (1 : 3 : 5), and *asymmetrical* (1 : 2 : 4). If the substituted radicles are of two different kinds, say chlorine and bromine, six isomerides may be formed, and if three different radicles are introduced, say chlorine, bromine, and NO_2, ten isomerides are possible.

Tetra-substitution derivatives of benzene may also be *adjacent* (1 : 2 : 3 : 4), *symmetrical* (1 : 2 : 4 : 5), and *asymmetrical* (1 : 3 : 4 : 5). With a single substituted radicle, only these three isomerides are possible, but two radicles may give 20, three radicles may give 16, and four radicles may give 30 tetra-substitution-products. Evidently only one penta-substitution-product is possible with one radicle.

The *experimental investigation of the orientation of a benzene derivative* consists in attempting to introduce fresh substituents into the nucleus, or in exchanging some substituent for hydrogen; how this settles the orientation will be understood from the following:

By treating a dibromobenzene with bromine it is possible to convert it into tribromobenzenes (though this means of converting a dibromo- into a tribromo-benzene is not the most convenient). It is found that the dibromobenzene which boils at 224° C. yields two tribromobenzenes, whilst that which boils at 219.5° C. yields three tribromobenzenes, and that which boils at 219° C. and melts at 89° C. (the others melt at about 1° C.) yields only one tribromobenzene. Now, an inspection of the formulæ for the three dibromobenzenes as written on the plane of the paper, will show that the 1 : 2-dibromobenzene can only yield two

tribromobenzenes, viz., 1 : 2 : 3 and 1 : 2 : 4, since 1 : 2 : 5 = 1 : 2 : 4 and 1 : 2 : 6 = 1 : 2 : 3. Again, it will be seen that the 1 : 3-dibromobenzene can yield three tribromobenzenes, viz., 1 : 2 : 3, 1 : 3 : 4 and 1 : 3 : 5 (1 : 3 : 6 = 1 : 3 : 4), whilst the 1 : 4-dibromobenzene can only yield one tribromobenzene, viz., 1 : 2 : 4 (or 1 : 3 : 4, or 1 : 4 : 5, or 1 : 4 : 6, all these being identical with 1 : 2 : 4). The diagram will make this more clear :—



It is evident that, of the three known dibromobenzenes, that must be the 1 : 2-derivative which yields two tribromo-derivatives; that the 1 : 3-derivative which yields three tribromo-derivatives; and that the 1 : 4-derivative which yields only one tribromo-derivative.

The orientation of tri-substitution derivatives may be similarly settled by exchanging one of the substituents for hydrogen, and thus obtaining one or more di-derivatives. If the derivative be the 1 : 2 : 3-derivative it will yield two di-derivatives, viz., 1 : 2 and 1 : 3; if it be the 1 : 3 : 5-derivative it can only yield one di-derivative.

The orientation of certain derivatives, which may be called standard derivatives, having been settled by investigations involving the principle stated above, the orientation of any new compound may be settled by converting it into one of these. Chief among these standards are the bromo-derivatives and the carboxylic acids (phthalic acid, &c.). Thus, the orientation of a newly discovered nitro-derivative could be settled by submitting it to a treatment (such as that indicated on p. 544) which would exchange the NO_2 groups for Br atoms; a study of the properties of the bromo-derivative thus produced would decide its orientation and therefore that of the original nitro-derivative.

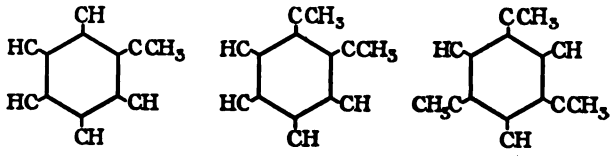
It is to be noticed that a polyvalent element can never be substituted for several hydrogen atoms in the benzene-nucleus; thus, C_6H_4O is not known.

The desire to prophesy what compound will be produced when a benzene derivative is treated with a substituting agent, has led to the formulation of several rules. Thus, it has been laid down that, when in a compound C_6H_5X, X is $\cdot NO_2$, $\cdot SO_2OH$ or $\cdot COOH$, any new radicle entering into C_6H_5X will take up the meta-position to X. If X be any other group, the newly entering substituent will generally produce the para-derivative, but accompanied by a little of the ortho- and sometimes of the meta-derivative.

If X be an element or radicle which forms a compound HX, capable of direct oxidation to HOX, the newly entering substituent will take the meta-position;

if, on the other hand, it be not so capable of oxidation, the newly entering substituent will take up the ortho- and para-positions (Crum Brown and Gibson). Thus, the introduction of a substituent into C_6H_5Cl will give ortho- and para-derivatives because HCl is incapable of direct oxidation to HOCl, whilst its introduction into $C_6H_5{\cdot}COOH$ will give a meta-derivative because HCOOH is capable of direct oxidation to $HO{\cdot}COOH$.

323. **Homologues of Benzene.**—These are derivatives of benzene containing alkyl radicles in place of hydrogen, such substituting radicles being termed *side-chains*. *Methylbenzene* (*toluene*), $C_6H_5{\cdot}CH_3$, *dimethylbenzenes* (*xylenes*), $C_6H_4(CH_3)_2$, *trimethylbenzenes*, $C_6H_3(CH_3)_3$ (see Fig. 263), and *tetramethylbenzenes*, $C_6H_2(CH_3)_4$, occur in coal-tar; numerous others, such as *ethylbenzene*, $C_6H_5{\cdot}CH_2{\cdot}CH_3$, *methylethylbenzene*, $C_6H_4(CH_3)(CH_2{\cdot}CH_3)$, &c., have been prepared synthetically.



Methylbenzene or toluene. 1:2-Dimethylbenzene or orthoxylene. 1:3:5-Trimethylbenzene or mesitylene.

Fig. 263.

The residues of the benzene hybrocarbons, or *aromatic radicles*, are named similarly to the alkyl radicles; thus, corresponding with methyl, ethyl, and propyl, there are *phenyl*, C_6H_5, *methylphenyl* or *tolyl*,* $C_6H_4{\cdot}CH_3$, *dimethylphenyl* or *xylyl*, $C_6H_3(CH_3)_2$.

Isomerism among these *alkylbenzenes* is similar to that among other substituted benzenes, except that there may be cases of isomerism in the side-chains. Thus there is only one methylbenzene and one ethylbenzene, but there are two propylbenzenes, one containing the normal propyl group, the other the iso-group (p. 567). These have the empirical formula C_9H_{12}, which also belongs to trimethylbenzene, of which there are three isomerides, as of other tri-substitution derivatives, and to methylethylbenzene, a di-substitution-product also existing in three forms.

Toluene and the *xylenes* are alone of any great practical importance among these homologues. They are extracted from the coal-tar obtained by the distillation of coal for the manufacture of coal-gas. A large quantity of the tar is distilled in an iron retort, when water passes over, holding salts of ammonia in solution, and accompanied by a brown, oily, offensive liquid which collects upon the surface of the water. This is the *light oil* containing the benzene hydrocarbons. To purify it, it is shaken with sulphuric acid, which removes aniline and other basic compounds, and afterwards with caustic soda, to dissolve carbolic acid (phenols). It is then subjected to a process of fractional distillation, similar in principle to the process described at p. 529.

* Much confusion is caused by modern nomenclature of hydrocarbon radicles. It was proposed to call radicles, such as tolyl and xylyl, *alphyl* radicles. Lately, however, this term has been applied to alkyl and substituted alkyl (benzyl) radicles, while tolyl, &c., have been termed *arryl* radicles, and benzyl, $C_6H_5{\cdot}CH_2$, xylylene, $C_6H_4(CH_2)_2$, &c., have been called *alpharryl* or *aralkyl* radicles.

Toluene, $C_6H_5{\cdot}CH_3$, is always present in commercial benzene. It was originally distilled from balsam of Tolu, and may be prepared by distilling *toluic acid*, $C_6H_4(CH_3)CO_2H$, with lime. It resembles benzene in odour, but it does not solidify even at − 20° C. It boils at 110° C. and its sp. gr. is 0.871. Benzene may be converted into toluene by first obtaining *bromobenzene*, C_6H_5Br, and treating this with methyl iodide and sodium, in the presence of ether, $C_6H_5Br + CH_3I + Na_2 = C_6H_5{\cdot}CH_3 + NaBr + NaI$. Under the action of oxidising-agents, toluene yields benzoic acid.

Toluene is used chiefly for making aniline dyes, and artificial oil of bitter almonds; it is also used as a solvent.

Xylene, $C_6H_4(CH_3)_2$, being a di-substitution-product, exists in three forms; but besides these there is a fourth hydrocarbon of the formula C_8H_{10}, namely, ethylbenzene, which, however, is a metameride of xylene. The portion of the light oil which distils at 136–141° contains about 70 per cent. of metaxylene (*isoxylene*), 20 per cent. of paraxylene, and 10 per cent. of orthoxylene. The mixture is used as a solvent.

By shaking the mixture with H_2SO_4 of 80 per cent. strength, the metaxylene is dissolved; by treating the residue with ordinary strong H_2SO_4, the orthoxylene is extracted leaving the paraxylene. The action of the H_2SO_4 is to convert the xylene into a sulphonic acid, $C_6H_3(CH_3)_2{\cdot}SO_2OH$, from which the hydrocarbon can be obtained by dilution with water and distillation. *Orthoxylene* boils at 142° C.; *metaxylene* at 139° C.; and *paraxylene* at 138° C. (m. p. 15° C.). By oxidation the methyl groups may be successively converted into COOH groups, yielding *toluic acids*, $C_6H_4(CH_3)(COOH)$, and *phthalic acids*, $C_6H_4(COOH)_2$, of each of which there are three, yielded respectively by ortho-, meta-, and paraxylene. Oxidising-agents do not act equally on the three isomerides, however. Chromic acid oxidises orthoxylene completely to CO_2 and H_2O, but converts para- and metaxalene into para- and metaphthalic acid respectively. Dilute HNO_3 oxidises the ortho- and paraxylene to ortho- and paratoluic acid respectively, while metaxylene is not attacked.

Mesitylene is 1 : 3 : 5-trimethylbenzene, $C_6H_3(CH_3)_3$, obtained by the action of sulphuric acid on acetone, $3(CH_3{\cdot}CO{\cdot}CH_3) = C_6H_3(CH_3)_3 + 3H_2O$, and by heating allylene with strong H_2SO_4, $3CH \vdots C{\cdot}CH_3 = C_6H_3(CH_3)_3$; it boils at 165° C. and is metameric with *cumene*, or *isopropylbenzene*, $C_6H_5{\cdot}CH(CH_3)_2$. *Durene* is 1 : 2 : 4 : 5-*tetramethylbenzene* (m. p. 79° C.) and has an odour of camphor; it is metameric with *cymene* or 1 : 4-*methylisopropylbenzene*, $C_6H_4(CH_3){\cdot}CH(CH_3)_2$, which is found in *oil of cummin* and is a product of the dehydration of camphor.

324. The chief *distinction between benzene hydrocarbons and open-chain hydrocarbons* resides in the ease with which the former may be converted into nitro-substitution-products by the action of strong nitric acid, and into sulphonic acids by the action of strong sulphuric acid. Moreover, the homologues of benzene easily undergo oxidation resulting in the conversion of the side-chains into the group *carboxyl*, COOH, characteristic of acids.

General methods for preparing benzene hydrocarbons are: (1) The distillation of the corresponding carboxylic acid with lime, which removes CO_2 from the carboxyl group: $C_6H_4(CH_3){\cdot}(COOH) = C_6H_5{\cdot}CH_3 + CO_2$. (2) The interaction of the bromo-substitution derivative and an alkyl iodide with sodium in ether: $C_6H_5{\cdot}Br + C_2H_5{\cdot}I + Na_2 = C_6H_5{\cdot}C_2H_5 + NaI + NaBr$ (*Fittig's* reaction, *cf.* the general methods for preparing paraffins, p. 531). (3) The interaction of a benzene hydrocarbon with an alkyl iodide in the presence of Al_2Cl_6, the precise function of which is not understood; $C_6H_5{\cdot}CH_3 + 2CH_3Cl = C_6H_3(CH_3)_3 + 2HCl$. (*Friedel* and *Crafts's* reaction.)

325. The above benzene hydrocarbons contain, as side-chains, the residues of saturated open-chain hydrocarbons. There also exist hydrocarbons containing residues of olefine and acetylene hydrocarbons. The *olefine-benzenes* correspond with the general formula C_nH_{2n-10}, and the *acetylene-benzenes* correspond with the general formula C_nH_{2n-12}.

Cinnamene, *styrolene*, or *styrene*, $C_6H_5 \cdot CH : CH_2$, is *phenyl-ethylene*. It is obtained by distilling cinnamic acid with lime; $C_6H_5 \cdot CH : CH \cdot COOH + Ca(OH)_2 = C_8H_8 + CaCO_3 + H_2O$. It can also be prepared by distilling balsam of storax, or by distilling the resin known as dragon's blood with zinc dust. Cinnamene is a fragrant liquid of sp. gr. 0.924, and boiling-point 145° C. It resembles the olefine hydrocarbons in uniting directly with chlorine, bromine, and iodine. When heated in a sealed tube to 200° C., it becomes a transparent solid known as *metacinnamene*, or *metastyrolene*, which is polymeric with cinnamene, into which it is reconverted by distillation. When heated with hydrochloric acid to 170° C., cinnamene is converted into *di-cinnamene*, $C_{16}H_{16}$.

Phenylacetylene, $C_6H_5 \cdot C \vdots CH$, a liquid boiling at 139° C., yields the explosive silver and copper derivatives characteristic of the true acetylenes (p. 538).

Hydroaromatic hydrocarbons. — When heated with hydriodic acid the aromatic hydrocarbons are converted into the corresponding hexamethylenes (p. 539); thus benzene yields hexamethylene (*hexahydrobenzene*, *benzenehexahydride* or *naphthene*), $H_2C\langle \begin{matrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{matrix} \rangle CH_2$, while toluene yields *methylhexamethylene* (*hexahydrotoluene* or *heptanaphthene*), $H_2C\langle \begin{matrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{matrix} \rangle CH \cdot CH_3$. These are colourless liquids, boiling at 81° C. and 103° C. respectively, and occur in Caucasian petroleum.

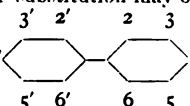
When monobromohexahydrobenzene is heated with quinolene it undergoes nucleal condensation, yielding *tetrahydrobenzene* (cylcohexene), $H_2C\langle \begin{matrix} CH_2 \cdot CH \\ CH_2 \cdot CH_2 \end{matrix} \rangle CH$, and when the dibromo-derivative of this is similarly treated, *dihydrobenzene* (*cyclohexadiene*), $HC\langle \begin{matrix} CH \cdot CH_2 \\ CH_2 \cdot CH \end{matrix} \rangle CH$, is obtained. The relation of these two compounds to benzene (*cyclohexatriene*) is apparent, and it will be seen that, if the formulæ are correct, cases of isomerism among the substitution derivatives should exceed those found among the corresponding benzene derivatives. For in both cases the character of the derivative may be expected to be influenced by the position of the double bond or bonds relatively to the substituent or substituents. Thus $H_2C\langle \begin{matrix} CH_2 \cdot CH \\ CH_2 \cdot CH_2 \end{matrix} \rangle CBr$ should differ from $H_2C\langle \begin{matrix} CH_2 \cdot CH_2 \\ CH : CH \end{matrix} \rangle CHBr$, and $HC\langle \begin{matrix} CH \cdot CH_2 \\ CH_2 \cdot CBr \end{matrix} \rangle CBr$ from $H_2C\langle \begin{matrix} CH_2 \cdot CH \\ CH : CBr \end{matrix} \rangle CBr$. Many such isomerides are known, and the nomenclature used to distinguish them consists in numbering the C atoms, as in benzene (No. 1 being always one to which a substituent is attached), and inserting the symbol Δ before the number of that C atom which is doubly linked to the one following it: thus the above bromo-derivatives are Δ 1-bromocyclohexene, Δ 5-bromocyclohexene, Δ 4, 6-orthodibromocyclohexene, and Δ 1, 5-orthodibromo cyclohexene, respectively.

326. **Hydrocarbons containing more than one benzene-nucleus.**—These hydrocarbons can be classified into several groups: (1) Those which contain benzene-nuclei directly united, such as *diphenyl*, $C_6H_5 \cdot C_6H_5$. (2) Those in which two or three nuclei are united by one carbon atom, as in *diphenyl-methane*, $C_6H_5 \cdot CH_2 \cdot C_6H_5$, and *triphenyl-methane*, $CH(C_6H_5)_3$. (3) Those which contain two benzene-nuclei united by two carbon atoms, like *dibenzyl*, $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot C_6H_5$. (4) Those which contain condensed nuclei, as explained under *naphthalene* and *anthracene*.

Many of the derivatives of these hydrocarbons are of importance in the arts, but, with the exception of those from naphthalene and anthracene, the hydrocarbons do not form the raw materials for making them.

Diphenyl or *phenyl-phenyl*, $C_6H_5 \cdot C_6H_5$, is prepared by the action of sodium on bromobenzene dissolved in ether; $2C_6H_5Br + 2Na_2 = (C_6H_5)_2 + 2NaBr$, a mode of

formation which settles its constitution. It may also be obtained by passing benzene vapour over red-hot pumice-stone; $2C_6H_5H=(C_6H_5)_2+H_2$; or by distilling potassium phenol with potassium benzoate, $C_6H_5{\cdot}OK+C_6H_5{\cdot}CO_2K=(C_6H_5)_2+K_2CO_3$; potassium oxalate may be substituted for benzoate, $2C_6H_5OK+(COOK)_2=(C_6H_5)_2+2CO(OK)_2$. It is also found among the last products of the distillation of coal-tar (at about 260° C.) Diphenyl crystallises from alcohol or ether in leafy crystals which have a pleasant odour and are insoluble in water. It fuses at 71° C., and boils at 254° C. When it is dissolved in glacial acetic acid, and treated with chromic acid, one of the C_6H_5 groups is destroyed, while the other forms benzoic acid, $C_6H_5{\cdot}CO_2H$. It forms numerous substitution derivatives, like benzene: since it may be regarded as already being a mono-substituted benzene, containing phenyl in the place of H, its mono-substitution derivatives will be di-substituted benzenes and occur in three isomeric modifications. Its di-derivatives occur in many forms, for substitution may occur in each ring. The orientation is expressed as follows:



Phenyl-tolyls, $C_6H_5{\cdot}C_6H_4{\cdot}CH_3$, and *ditolyls*, $C_6H_4(CH_3){\cdot}C_6H_4(CH_3)$, are examples of mono- and di-substituted diphenyl; the 4- and 4 : 4′-derivatives are the most common. By treating a mixture of 1 : 4-$C_6H_4Br_2$ and C_6H_5Br with sodium, 1 : 4-*diphenylbenzene*, $C_6H_4(C_6H_5)_2$, is obtained; it melts at 205° C.

Diphenylmethane (*benzylbenzene*), $C_6H_5{\cdot}CH_2{\cdot}C_6H_5$. It is obvious that toluene may be regarded as phenylmethane, $CH_3(C_6H_5)$, and just as toluene may be prepared by the interaction of methyl chloride and benzene in presence of Al_2Cl_6, so diphenylmethane, $CH_2(C_6H_5)_2$, can be prepared from phenylmethyl chloride, commonly called benzyl chloride (*q.v.*), $C_6H_5{\cdot}CH_2Cl$, and benzene in presence of Al_2Cl_6; $C_6H_5H+C_6H_5{\cdot}CH_2Cl=C_6H_5{\cdot}CH_2{\cdot}C_6H_5+HCl$. It crystallises in needles which smell like the orange and dissolve in alcohol and ether; it melts at 26° C. and boils at 261° C. Chromic acid oxidises it to diphenyl-ketone (*q.v.*). When passed through a red-hot tube it undergoes the same kind of condensation as benzene does when it yields diphenyl (p. 550) under the same conditions; the product, *diphenylene-methane** or *fluorene*, $\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\!\!>\!CH_2$, is found in the last runnings (300° – 305° C.) from coal-tar and crystallises from alcohol with a blue fluorescence. Oxidation converts it into diphenylene ketone. It melts at 113° C. and boils at 295° C. *Triphenylmethane*, $CH(C_6H_5)_3$, is obtained by the interaction of chloroform and benzene in presence of Al_2Cl_6: $3C_6H_5H+CHCl_3=CH(C_6H_5)_3+3HCl$. It crystallises in colourless prisms, which when formed from a benzene solution contain one molecule of *benzene of crystallisation*. It dissolves in hot alcohol, melts at 93° C., and boils at 359° C. The aniline dyes are derivatives of this hydrocarbon.

Dibenzyl, $C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_5$. Toluene can give rise to two hydrocarbon residues or radicles, viz., tolyl, $C_6H_4{\cdot}CH_3$, and benzyl, $C_6H_5{\cdot}CH_2$. When the chloride of the latter radicle is treated with sodium, dibenzyl is produced, $2(C_6H_5{\cdot}CH_2Cl)+Na_2=C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_5+2NaCl$. It may also be regarded as *diphenylethane*; it melts at 52° C. and boils at 284° C.; when oxidised it yields benzoic acid. *Diphenylethylene*, or *stilbene*, or *tolylene*, $C_6H_5{\cdot}CH:CH{\cdot}C_6H_5$, is formed by treating benzal chloride (*q.v.*) with sodium; $2C_6H_5{\cdot}CHCl_2+Na_2=C_6H_5{\cdot}CH:CH{\cdot}C_6H_5+2NaCl$. Also by partially oxidising toluene or dibenzyl, by passing it over hot PbO. It crystallises in prisms, melts at 125° C., boils at 306° C. and dissolves in hot alcohol. It contains true ethylenic linking, for the first action of bromine on it is the formation of the dibromide $C_6H_5{\cdot}CHBr{\cdot}CHBr{\cdot}C_6H_5$. *Diphenylacetylene* or *tolane*, $C_6H_5{\cdot}C\equiv C{\cdot}C_6H_5$, is formed by boiling stilbene dibromide with alcoholic potash. It melts at 60° C., and behaves as an acetylene, save that, not containing a $C\equiv CH$ group it yields no metallic derivative. *Diphenyldiacetylene*, $C_6H_5{\cdot}C\equiv C{\cdot}C\equiv C{\cdot}C_6H_5$, is of importance as the hydrocarbon from which indigo is descended; it melts at 88° C.

327. **Naphthalene**, $C_{10}H_8$, is a crystalline hydrocarbon with an odour of coal-gas, and is occasionally deposited in gas-pipes in cold weather, causing an obstruction. It is a very common product of the action of a

* $(C_6H_4)''$ is called phenylene, by analogy with $(C_2H_4)''$, ethylene.

high temperature upon substances rich in carbon; coal and wood yield it on distillation; marsh-gas, alcohol vapour, and ether vapour, when passed through a red-hot tube, deposit crystals of naphthalene in the cooler part. Burmese petroleum and Rangoon tar contain naphthalene.

When coal-tar is distilled, the benzene hydrocarbons which distil over in the *light-oil*, are succeeded, as the temperature rises, by a yellow oil which is heavier than water. This, known as *dead-oil*, is much more abundant than the light-oil, amounting to about one-fourth of the weight of the tar, and containing those constituents of the tar which have a high specific gravity and boiling-point. When the temperature has risen to about 200° C., the distilled liquid partly solidifies on cooling, from the crystallisation of naphthalene. This portion is pressed to expel the liquid part, washed successively with caustic soda and sulphuric acid, and distilled; or the washed naphthalene may be sublimed.

Properties.—Transparent crystals, smelling of gas, melting at 80° C., and inflammable, burning with a smoky flame. It sublimes much below its boiling-point (218° C.). Insoluble in water, soluble in alcohol, ether, and benzene.

In its chemical relations, naphthalene is closely connected with benzene, but it shows a greater disposition to form addition-products with chlorine and bromine, with which it also yields numerous substitution-products. Naphthalene absorbs chlorine, forming a yellow liquid, *naphthalene dichloride*, $C_{10}H_8Cl_2$, and a crystalline solid, *naphthalene tetrachloride*, $C_{10}H_8Cl_4$. The non-existence of $C_{10}H_8Cl_3$ is in accordance with the law of even numbers (p. 523).

Naphthalene is used for making phthalic acid, into which it is converted by oxidation; for increasing the illuminating value of coal-gas (*albo-carbon* light); and as an insecticide. Many of its derivatives are used for making synthetic dyes.

Constitution of naphthalene.—The similarity of the behaviour of naphthalene with that of benzene indicates an analogous structure for these two compounds, and since when it is oxidised naphthalene yields a benzene dicarboxylic acid, $C_6H_4(COOH)_2$, it must be assumed to contain a benzene ring. Thus, six of the ten carbon atoms are accounted for: two of the remaining four must be attached directly to two of the carbon atoms of the benzene ring, otherwise a dicarboxylic acid could not have been obtained by oxidation; moreover, since the dicarboxylic acid proves to be phthalic acid, which is believed to have the carboxyl groups attached to adjacent carbon atoms of the ring, the two carbon atoms must be attached to the benzene ring in the ortho-position to each other. The two remaining carbon atoms are believed to form a closed chain with the two just considered. Postponing, for the moment, the evidence for this belief, the formula to which it gives rise may be regarded as consisting of two benzene rings, so condensed together that they have two carbon atoms in common. Fig. 264 furnishes a representation of the structure of naphthalene (the H atoms, attached one to each numbered C atom, having been omitted) and at the same time indicates the numbering of the carbon atoms for purposes of orientation. To avoid the representation of ethylenic linking (*cf* p. 546) many chemists omit the five double bonds in the formula. The Greek letters are sometimes used instead of the numbers.

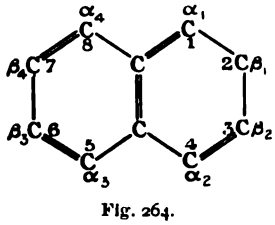


Fig. 264.

That naphthalene consists of two benzene-nuclei condensed as represented by the formula is supported by the following facts:—When nitronaphthalene is oxidised nitrophthalic acid, $C_6H_3(NO_2)(COOH)_2$, is produced; from this reaction it is evident that the nitro-group in nitronaphthalene is in a benzene ring, whether

there be a second benzene ring or not, and we may suppose that it occupies the position 8 in the formula (Fig. 264). By reducing the nitronaphthalene it becomes amidonaphthalene, that is, the nitro-group has become an amido-group, and it is reasonable to suppose that the new group occupies the same position as the nitro-group did. Now if this amidonaphthalene be oxidised it is not an amidophthalic acid which is obtained, but simply phthalic acid itself; since an oxidising action cannot substitute H for NH_2, it must be concluded that it is the ring in which the NH_2 group was situated that has been removed by the oxidation, and yet a benzene ring compound (phthalic acid) has been left, showing that the naphthalene must contain two such rings.

It is found that two isomerides of every mono-substitution product of naphthalene exist: this is in accord with the formula, for it will be seen that whilst the carbon atoms 1, 8, 4 and 5, are similarly situated towards the whole molecule, they are differently situated from 2, 3, 6 and 7, which, however, are similarly situated towards the molecule. When a substituent takes up any of the first-named positions, it is termed an α-derivative, whilst the other positions yield β-derivatives. It will be found that 10 di- and 14 tri-derivatives are possible; all the mono-, di-, and tri-chloronaphthalenes are known and orientated, so that the orientation of a new derivative may be settled by its conversion into one of these. The 1 : 8-derivatives are sometimes called peri-derivatives.

The general expression for the *naphthalene hydrocarbons* would be C_nH_{2n-12}. Examples of members of the homologous series are *methyl-naphthalenes*, $C_{10}H_7{\cdot}CH_3$, and *ethyl-naphthalenes*, $C_{10}H_7{\cdot}C_2H_5$. These are liquid even at low temperatures, and are constituents of coal-tar.

Ethene-naphthalene, or *acenaphthene*, $C_{10}H_6\begin{cases}CH_2\\CH_2\end{cases}$, which is found in small quantity in coal-tar is obtained by passing vapour of α-ethyl-naphthalene through a red-hot tube, when hydrogen is separated. It forms colourless prisms (m.-p. 95° C.: b.-p. 277°).

Acetylene-naphthalene, $C_{10}H_6\begin{cases}CH\\CH\end{cases}$, is obtained as a fusible solid (92° C.) by passing vapour of acenaphthene over red-hot lead oxide, which removes H_2.

Dinaphthyl, $C_{10}H_7{\cdot}C_{10}H_7$, is produced when vapour of naphthalene is passed through a red-hot tube, by the oxidising action of MnO_2 with H_2SO_4 on naphthalene, and by treating $C_{10}H_7Br$ with Na. It forms scaly crystals, m.-p. 154° C.

The naphthalenes behave in a rather characteristic way with picric acid. If they be dissolved in hot alcohol and mixed with a hot solution of picric acid in alcohol, stellate tufts of yellow or red needles are deposited on cooling. These consist of a compound of single molecules of the naphthalene and picric acid.

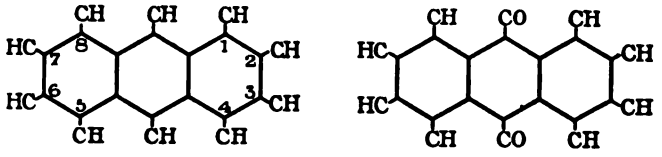
Hydronaphthalenes.—Like the aromatic hydrocarbons, naphthalene readily forms hydrogen addition-products when treated with nascent hydrogen or hydriodic acid. These products range from *dihydronaphthalene*, $C_{10}H_{10}$ to *dodekahydronaphthalene*, $C_{10}H_{18}$, in which all the double bonds have been converted into single bonds, leaving the molecule capable of attaching 10 atoms of H. When the hydrogenisation is in one ring only—which is the case with the di- and the tetra-hydronaphthalenes most easily obtained—the hydrogenised ring has properties resembling those of an open-chain hydrocarbon, so that the molecule is more like a phenyl derivative, having an open side-chain, than a naphthalene. The substitution derivatives of such hydronaphthalenes are therefore distinguished as *aromatic* (ar-) or *alicyclic* (ac-) accordingly as the substituent is in the phenyl ring or the hydrogenised ring. Thus $C_6H_4 : C_4H_7(NH_2)$ is ac-amidotetrahydronaphthalene, $C_6H_3(NH_2) : C_4H_8$ is ar-amidotetrahydronaphthalene, while $C_6H_3(NH_2) : C_4H_7(NH_2)$ is an ar-ac-derivative.

328. **Anthracene,** $C_{14}H_{10}$, is found among the last products of the distillation of coal-tar (especially from Newcastle coal), and may be distinguished from naphthalene by its being almost insoluble in alcohol and fusing only at 213° C. It crystallises in colourless tables having a blue fluorescence, and boils at 351° C. That fraction of the coal-tar distillate which comes over at about 360° C. solidifies on cooling to a mass of crude anthracene. It is freed from liquid hydrocarbons by

pressure, washed with light petroleum, and purified by crystallisation from hot benzene, or by sublimation as for naphthalene. Commercial anthracene is employed for the manufacture of alizarin.

Anthracene is formed when vapour of toluene is passed through a red-hot tube containing pumice-stone to expose a large heated surface ; $2C_7H_8 = C_{14}H_{10} + 3H_2$. Lead oxide, by oxidising the H, effects the change at a lower temperature. It absorbs chlorine, forming crystals of *anthracene dichloride*, $C_{14}H_{10}Cl_2$, and *chloranthracene*, $C_{14}H_9Cl$. With nitric acid, anthracene behaves in a different way from benzene and naphthalene, showing less disposition to the formation of nitro-compounds. When heated with nitric acid it undergoes oxidation and is converted into a yellow crystalline body called *anthraquinone*, $C_{14}H_8O_2$ or $(C_6H_4)_2(CO)_2$.

Constitution of anthracene.—From the fact that anthracene can be obtained synthetically from benzene and tetrabromethane in the presence of Al_2Cl_6, it is concluded that this hydrocarbon has a constitution represented by the formula $C_6H_4\langle\begin{smallmatrix}CH\\ \cdot\\ CH\end{smallmatrix}\rangle C_6H_4$: thus, $C_6H_6 + \begin{smallmatrix}BrCHBr\\ \cdot\\ BrCHBr\end{smallmatrix} + C_6H_6 = C_6H_4\langle\begin{smallmatrix}CH\\ \cdot\\ CH\end{smallmatrix}\rangle C_6H_4 + 4HBr$.



Anthracene. Anthraquinone.

Fig. 265.

The C_6H_4 groups constitute two benzene rings (Fig. 265), whilst the central carbon atoms may be regarded as the residue of a third ring which has two carbon atoms in common with each of the other rings. By treatment with hydrogenising agents (hydriodic acid, for example) the para-union between the central carbon atoms may be opened up and *dihydroanthracene* or *anthracene dihydride*, $C_6H_4\langle\begin{smallmatrix}CH_2\\ \\ CH_2\end{smallmatrix}\rangle C_6H_4$, formed. Support is lent to this formula for anthracene by the synthesis of anthraquinone (*q.v.*).

The orientation of anthracene-substitution-products is expressed similarly to that of naphthalene derivatives. Three mono-substitution-products are possible—viz., the α- and β-, like the α- and β-naphthalene derivatives, and the γ- or *meso*-derivatives, containing a substituent in place of the H of one of the middle carbon atoms, which may be numbered 9 and 10.

Paranthracene $(C_{14}H_{10})_2$, crystallises in plates from a cold saturated solution of anthracene in benzene exposed to sunshine. It does not fuse until heated to 244° C., when it is converted into anthracene. Bromine and nitric acid attack it with difficulty.

Phenanthrene, $C_{14}H_{10}$, is isomeric with anthracene, which it accompanies in coal-tar. It is more soluble in petroleum spirit and in alcohol than is anthracene; the former solvent serves to separate it from the bulk of the crude anthracene, the separation being finished by fractional distillation. It is used for making blacks. It melts at 99° C., and boils at 340° C.

Phenanthrene is formed when stilbene or orthoditolyl is passed through a red-hot tube ; since stilbene is known to contain ethylenic linked carbon (p. 546), and ditolyl to be a diphenyl derivative, it is concluded that phenanthrene has the constitution $\begin{smallmatrix}C_6H_4\cdot CH.\\ \cdot\\ C_6H_4\cdot CH\end{smallmatrix}$, which is confirmed by the fact that its oxidation yields *diphenic acid*, $\begin{smallmatrix}C_6H_4\cdot COOH\\ \cdot\\ C_6H_4\cdot COOH.\end{smallmatrix}$

Retene, $C_{18}H_{18}$, is a *methylisopropylphenanthrene* found in wood-tar.

Chrysene, $\begin{smallmatrix}C_6H_4 - CH\\ \cdot\\ C_{10}H_6 - CH\end{smallmatrix}$, and *picene*, $\begin{smallmatrix}C_{10}H_6 - CH\\ \cdot\\ C_{10}H_6 - CH\end{smallmatrix}$, which contain the naphthylene

group $C_{10}H_8$, are similar to anthracene in properties. The former melts at 250° C. and boils at 448° C. ; it is a final product in coal-tar distillation, and owes its name to its yellow colour in the crude state ; when purified it is white with a violet fluorescence. Picene melts at 364° C., a higher melting-point than that of any other hydrocarbon ; it is found in the tar from lignite, and is highly insoluble. *Fluoranthrene* (*idryl*), $C_{15}H_{10}$, and *pyrene*, $C_{16}H_{10}$, occur in "stubb" or "stupp," the unctuous matter which distils during the winning of mercury from Idrian ores.

329. **Terpene Hydrocarbons.**—*Oil of turpentine*, $C_{10}H_{16}$, is obtained by distilling the viscous exudation procured by cutting into the bark of various species of pine. Several varieties of turpentine are met with in commerce, of which the two best known are the common turpentine which is obtained from the Scotch fir, and Venice turpentine from the larch. These are both solutions of *colophony*, or common rosin, in oil of turpentine, and, when distilled, yield from 75 to 90 per cent. of rosin, which remains in the still, and from 25 to 10 per cent. of the oil, commonly sold as *spirits of turpentine*.

The oil of turpentine boils at 158°—160° C., and has the sp. gr. 0.864. It is very sparingly soluble in water, but dissolves in alcohol and ether. It burns with a smoky luminous flame. Its property of dissolving resins and fats renders it useful in preparing paints and varnishes. It is also a good solvent for caoutchouc.

Oil of turpentine is the representative of a large class of hydrocarbons called the *terpenes*, derived like itself from the vegetable kingdom. All the members of this group contain the same proportions of carbon and hydrogen, and the greater number have the same molecular formula as turpentine, $C_{10}H_{16}$. The terpenes resemble each other in their liability to suffer conversion into isomerides, in their optical activity (p. 542), in their solidification by absorption of oxygen when exposed to air, in their combination with water to form crystalline hydrates, and, above all, in their tendency to combine with hydrochloric acid to form crystalline compounds.

The essential oils of *bergamotte*, *birch*, *chamomile*, *caraway*, *hops*, *juniper*, *lemons*, *myrtle*, *nutmeg*, *orange*, *parsley*, *pepper*, *savin*, *thyme*, *tolu*, and *valerian* are all terpenes (for the most part mixtures of terpenes) of the formula $C_{10}H_{16}$, accompanied by its oxygenated derivatives (alcohols, aldehydes, and ketones).

Essential *oil of poplar* is a *di-terpene*, $C_{20}H_{32}$. The oils of *calamus*, *cascarilla*, *cloves*, *cubebs*, *patchouli*, *cedar*, and *rosewood* are *sesqui-terpenes*, $C_{15}H_{24}$.

The essential oils are generally extracted from the flowers, fruit, leaves, or seeds, by distillation with water, the portion of the plant selected being suspended in the still by means of a bag or cage, to prevent it from being scorched by contact with the hot sides of the still, and so contaminating the distillate with *empyreumatic* matters. The water which distils over always holds a little of the essential oil in solution, and it is in this way that the fragrant distilled waters of the druggist are obtained. When the essential oil is present in large proportion, it collects as a separate layer on the surface of the water, from which it is easily decanted. The oil which is dissolved in the water may be separated from it by saturating the liquid with common salt, when the oil rises to the surface ; or by shaking it with ether, which dissolves the oil and separates from the water, the ethereal solution floating on the surface, and leaving the oil when the ether is distilled off.

In cases like that of jasmine, where the delicate perfume of the flower would be injured by a high temperature, the flowers are pressed between woollen cloths saturated with oil of poppy-seeds, which thus acquires a powerful odour of the flower. Carbon bisulphide is also sometimes employed as a solvent for extracting the essential oils.

330. The terpenes are all polymerides of the formula C_5H_8. A hydrocarbon having this molecular formula and belonging to the diolefines (p. 537) is called *isoprene* (b.-p. 37° C.), and appears to have the constitution $CH_2 : C(CH_3)\cdot CH : CH_2$ (*methyldivinyl*): many terpenes yield isoprene (*hemiterpene*) when heated, and isoprene polymerises to dipentene.

A few terpenes of minor importance, except that they are the hydrocarbons corresponding with some valuable essential oils, appear to be open-chain compounds of the olefine, diolefine and triolefine series. *Rhodinol*, $C_{10}H_{20}O$, and *geraniol*, $C_{10}H_{18}O$, are alcohols belonging to these terpenes, and are constituents of the oils of geranium, roses, and pelargonium: *linalool*, $C_{10}H_{18}O$, is a similar alcohol from the oils of lavender, bergamotte, limes, and marjoram. *Citral*, $C_{10}H_{16}O$, is an aldehyde found in lemon oil, lemon-grass oil, and verbena oil. By shaking a mixture of citral and acetone with baryta water and distilling, an oil, *pseudoionone*, $C_{13}H_{20}O$, is obtained: this open-chain ketone is converted by treatment with sulphuric acid into a hydroaromatic ketone of the same molecular formula, *ionone*, the odour of which resembles that of the oil from the root of the violet. Ionone is made in the above manner and sold as "artificial oil of violets."

The majority of the terpenes, however, appear to be cyclic compounds and fall into two classes accordingly as they absorb two or four atoms of bromine, indicating one or two ethylenic linkings respectively in the molecule. Those which absorb four atoms of bromine comprise *limonene*, *dipentene*, *sylvestrine*, and *terpinolene* as chief members. They yield 1 : 4-benzenedicarboxylic acid (terephthalic acid) when oxidised, thus indicating that they contain a benzene nucleus which probably has two alkyl groups in the 1 : 4-positions. Moreover, when dehydrogenised they yield cymene, which is 1 : 4-methylisopropylbenzene (p. 549), and contains two H atoms fewer than the terpenes contain. These terpenes appear, therefore, to be isomeric modifications of *dihydrocymene*,

$$CH_3.C\begin{matrix}CH & -CH_2\\ CH_2 & -CH_2\end{matrix}\!\!>C=C(CH_3)_2.$$

The terpenes which absorb only two atoms of bromine, and have therefore only one ethylenic linking, are closely related to camphor (*q.v.*), the constitution of which has been much discussed; the chief are *pinene*, *camphene*, and *fenchene*.

Two terpenes *terpinene* and *phellandrene*, do not appear to contain ethylenic linking, as they do not combine with bromine. They combine with N_2O_3.

The terpenes boil at about the same temperature (155°—180° C.), so that their separation by fractional distillation is not possible, and fractional crystallisation of some of their compounds is the only available method of purifying them. Most of them combine with NOCl to form crystalline compounds, $C_{10}H_{16}\cdot NOCl$, nitrosochlorides.

Limonene exists in two forms: *Dextrolimonene* (*citrene*, *hesperidene*, *carvene*) occurs in oil of orange-peel and, with pinene, in oil of citron: it boils at 175° C. and has sp. gr. 0.846. *Lævolimonene* has the same properties, except that, as its name implies, it rotates the plane of polarised light in the opposite direction: it occurs with lævopinene in "oil of fir-wool." Each limonene yields two nitrosochlorides, which are isomerides, differing only in their physical properties. When equal volumes of the two limonenes are mixed, *dipentene* (*cinene*) is produced: this has no action on polarised light; it is found with sylvestrene in Russian and Swedish turpentine, and is a product of the destructive distillation of caoutchouc and of the polymerisation of isoprene; acids convert it into terpinene.

Sylvestrene (b.-p. 176° C.) is a very stable terpene, known only in a dextro-form: it is characterised by giving a blue colour with acetic anhydride and strong H_2SO_4.

Terpinolene (b.-p. 183° C.), obtained by heating terpineol (*q.v.*) with oxalic or formic acid, has not been found in nature.

Terpinene (b.-p. 180° C.), found in oil of cardamoms, is one of the most stable compounds of this group, and, with *phellandrene* (b.-p. 170° C.), which occurs in dextro- and lævo-form, is characterised by its compound with N_2O_3 (nitrosite).

Pinene (*terpene*) is the chief constituent of turpentine oil, the *dextropinene* (*australene*) being characteristic of American and English turpentine, and *lævopinene* (*terebenthene*) of French turpentine; an *inactive pinene* has also been obtained. All three forms boil at 155° C. When HCl is passed into oil of turpentine, well-cooled, *dextropinene hydrochloride*, $C_{10}H_{17}Cl$, is obtained. This is called *artificial camphor*, since it resembles the natural product in its crystals and its odour; it melts at 125° C. and boils at 208° C., and is optically inactive, though the hydrochloride from lævopinene is laevo-rotatory.

Camphene is solid, melting at 48° C. and boiling at 160° C. It occurs in three optical modifications, and is prepared by heating pinene hydrochloride with a feeble alkali (aniline); it has been detected in oil of ginger and citronella oil. On oxidation it yields camphor.

Fenchene, from oil of fennel, exists in the usual three optical modifications, which boil at about 150° C.

Hydroterpenes are also known. Chief among them is *menthene*, $C_{10}H_{18}$, obtained from *oil of peppermint*. B.-p. 169° C.

331. **Caoutchouc**, or india-rubber, may be classed among the terpene hydrocarbons, its chief constituent (a so-called *polyprene*) having the empirical formula C_5H_8, but a molecular formula $(C_5H_8)_n$. It is procured from a milky exudation furnished by several tropical plants, particularly by the *Hævea guianensis* and *Jatropha* or *Siphonia elastica*. Incisions are made in these trees, and the milky liquid thus obtained is spread upon a clay bottle-shaped mould, which is then suspended over a fire; a layer of caoutchouc is thus deposited, and its thickness is afterwards increased by repeated applications of the milky liquid, the mould being eventually broken out of the caoutchouc bottle thus formed. The dark colour of commercial india-rubber is believed to be due to the smoke from the fire over which it is dried, for pure caoutchouc is white, and may be obtained by dissolving india-rubber in chloroform, and precipitating with alcohol; the precipitate forms a gummy mass when dried. Commercial india-rubber contains a small quantity of albumin, derived from the original milky liquid, this being really a solution of albumin holding in suspension about 30 per cent. of caoutchouc, which rises to the surface like cream when the juice is mixed with water and allowed to stand, becoming coherent and elastic when exposed to air. It will be remembered that many of the chief uses of caoutchouc depend upon its physical rather than upon its chemical properties, its lightness (sp. gr. 0.93) and impermeability to water adapting it for waterproof clothing, life-buoys, &c., while its remarkable elasticity gives rise to a still greater variety of applications.

For the manufacture of *waterproof cloth* caoutchouc is dissolved in rectified turpentine, and the solution is spread, in a viscid state, over the surfaces of two pieces of cloth of the same size, which are then laid face to face and passed between rollers, the pressure of which causes perfect adhesion between the surfaces. *Waterproof felt* is made by matting together fibres of cotton impregnated with a solution of caoutchouc in naphtha, and passing the felt between rollers. When kept for a long time, its strength and waterproof qualities are deteriorated, in consequence of the oxidation of the caoutchouc, which is thus converted into a resinous substance resembling shell-lac and easily dissolved by alcohol.

Caoutchouc is slowly dissolved by carbon disulphide, benzene, chloroform, coal-naphtha, petroleum, turpentine, and the fixed oils.

Marine glue is a solution of caoutchouc with a little shell-lac in coal-naphtha.

The alkalies and diluted acids are without action on caoutchouc. When gently warmed, it becomes far more soft, pliable, and extensible; it fuses at about 250° F. (121° C.) to an oily liquid, which becomes viscid on cooling, but will not solidify, and is useful for lubricating stop-cocks. When further heated in air, it burns with a bright smoky flame. Heated in a retort, caoutchouc is decomposed

into several hydrocarbons, among which are isoprene, dipentene (*caoutchene*), and *hevеene*, a sesquiterpene, $C_{15}H_{24}$ (b.-p. 260° C.).

Vulcanised rubber, the chemical constitution of which is not understood, is produced by incorporating india-rubber with 2 or 3 per cent. of sulphur, which not only greatly increases its elasticity, but prevents it from cohering under pressure, and from adhering to other surfaces unless strongly heated. It also becomes insoluble in turpentine and naphtha. Ordinary vulcanised rubber generally contains more sulphur than is stated above, which causes it to become brittle after a time: for some purposes, such as the manufacture of overshoes, other substances are added besides sulphur, such as lead carbonate and zinc oxide.

When a sheet of caoutchouc is allowed to remain for some time in fused sulphur at 120° C., it absorbs 12 or 15 per cent. without any material alteration, but if it be heated for a short time to 150° C. it becomes vulcanised; and when still further heated, is converted into the black horny substance called *vulcanite* or *ebonite*, and used for the manufacture of combs, &c., and as an electrical insulator.

Vulcanised caoutchouc is sometimes made by mechanically incorporating the sulphur with india-rubber softened by heat; or by immersing the rubber in a mixture of sulphur with chloride of lime, or in carbon disulphide mixed with 2.5 per cent. of S_2Cl_2. It can also be made by dissolving the sulphur in turpentine, which is afterwards used to dissolve the caoutchouc; when the turpentine has evaporated, a mixture of caoutchouc and sulphur is left, which may be easily moulded into any required shape, and afterwards vulcanised by exposure to high-pressure steam having a temperature of about 140° C.

By treating vulcanised caoutchouc with sodium sulphite, the excess of sulphur above 2 or 3 per cent. may be dissolved out. The whole of the sulphur may be removed, and the caoutchouc devulcanised, by boiling with a 10 per cent. solution of caustic soda.

Caoutchouc is by no means rare in the vegetable world, being found in the milky juices of the poppy (and thence in the opium), of the lettuce, and of the *euphorbium* and *asclepia* families.

Gutta-percha (empirical formula C_5H_8), like caoutchouc, is originally a milky exudation from incisions made into the wood of the *Isonandra percha*, a native of the Eastern Archipelago. This juice soon solidifies, when exposed to air, to a brown mass heavier than caoutchouc (sp. gr. 0.98) and differing widely from it by being tough and inelastic when cold, and becoming quite soft and plastic when heated nearly to the boiling-point of water. Being impervious to water, it is used as a waterproof material and for water-pipes, and its want of conducting power for electricity is turned to account for insulating telegraph cables.

Gutta-percha is dissolved by those substances which dissolve caoutchouc. It is not affected by diluted acids and alkalies, and is used for keeping hydrofluoric acid. It melts easily, and is afterwards decomposed, yielding products similar to those from caoutchouc.

Commercial gutta-percha contains only about 80 per cent. of the hydrocarbon, which may be dissolved out by boiling with ether; the solution, when evaporated, leaves the hydrocarbon as a white powder fusing at 100° C. The portion insoluble in ether contains two resinous bodies soluble in boiling alcohol, which deposits, on cooling, a white crystalline resin, of the empirical formula $C_{10}H_{16}O$, and retains in solution an amorphous resin, $C_{20}H_{32}O$. The existence of these bodies renders it probable that gutta-percha is $C_{20}H_{32}$, the crystalline resin being $C_{20}H_{32}O_2$. Exposure to air and light gradually converts pure gutta-percha into these resinous bodies.

332. **Camphors.**—Closely allied to the essential oils are the different varieties of camphors, which are formed by oxidation of the hydrocarbons contained in the essential oils. Recently they have been shown to be alcohols or ketones, and in a strict classification should receive notice

under these headings. Their natural connection with the parent hydrocarbons, however, warrants their consideration here.

Menthol or *menthocamphor*, $C_{10}H_{20}O$, is a secondary alcohol, forming the chief constituent of oil of peppermint; its relationship to cymene (p. 549), is indicated by the formula, $CH_3{\cdot}CH\langle\begin{matrix}CH_2{\cdot}CHOH\\CH_2{\cdot}CH_2-\end{matrix}\rangle CH{\cdot}CH(CH_3)_2$. It melts at 42° C. and boils at 212° C.; it is used for external application as an anti-neuralgic. Heated with dilute H_2SO_4 it yields menthene, and by oxidation it becomes *menthone*, a ketone differing from menthol in that CO is substituted for CHOH in the above formula, and also occurring in oil of peppermint. It boils at 206° C. and occurs in dextro- and lævo-form.

Terpin, $C_{10}H_{18}(OH)_2$, is a dihydric alcohol existing in a cis- and trans-form (see *fumaric acid*); the former melts at 104° C., boils at 258° C., and combines readily with one mol. H_2O to form *terpin hydrate* (m.-p. 117° C.), which is a product of the action of dilute acids on turpentine, limonene, and dipentene. Trans-terpin melts at 157° C., boils at 264° C., and forms no hydrate. When terpin hydrate is heated with dilute acid it yields, besides *cineol*, $C_{10}H_{18}O$ (the chief constituent of eucalyptus oil), dipentene, &c., *terpineol*, a monohydric alcohol melting at 35° C., and probably $CH_3C\langle\begin{matrix}CH{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}\rangle CH{\cdot}C(OH)(CH_3)_2$. An isomeric terpineol melts at 69° C.

Carrone or *carvol*, $C_{10}H_{14}O$, boils at 225° C., and occurs in dextro-, lævo-, and inactive form, like limonene, to which it is closely related. It is probably a ketone of the form $CH_3C{\cdot}\langle\begin{matrix}CH{\cdot}CH_2\\CO{\cdot}CH_2\end{matrix}\rangle CH{\cdot}C\langle\begin{matrix}CH_3\\CH_2\end{matrix}$, differing from limonene by having O in place of H_2. d-Carvone occurs in *kümmel oil* and *oil of dill*, and when heated with KOH, becomes 1 : 4 : 2-methylisopropylphenol, or carvacrol (*q. v.*).

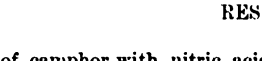
Japan or common camphor ($C_{10}H_{16}O$) is found deposited in minute crystals in the wood of the *Laurus camphora*, or camphor laurel, from which it is obtained by chopping up the branches and distilling them with water in a still, the head of which is filled with straw, whereon the camphor condenses. It is purified by subliming it in large glass vessels containing a little lime.

Camphor passes into vapour easily at the ordinary temperature of the air, and is deposited in brilliant octahedral crystals upon the sides of the bottles in which it is preserved. It fuses at 347° F. (175° C.), and boils at 399° F. (204° C.), and is very inflammable, burning with a bright smoky flame. It is sometimes dissolved in the oil used for the lamps of magic-lanterns, to increase its illuminating power. Camphor is lighter than water (sp. gr. 0.985), and whirls about upon its surface in a remarkable way, dissolving meanwhile very sparingly (1 part in 1000), alcohol and ether being its appropriate solvents.

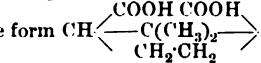
An alcoholic solution of ordinary camphor is dextro-rotatory, but the camphor from some species of *Matricaria* is lævo-rotatory. When the two are mixed an inactive camphor is produced.

When distilled with P_2O_5 ordinary camphor yields cymene, $C_{10}H_{14}$, and when heated with iodine it yields carvacrol, $C_{10}H_{14}O$. The former is 1 : 4-methyliso-propylbenzene of which carvacrol is the hydroxy-derivative, the OH group being in the 2-position. It would seem from this that camphor must be derived from a benzene ring having a methyl, an isopropyl, and an oxygen atom in the 1 : 4 : 2-positions respectively. The oxygen does not appear to be present as an OH group, but rather as a ketonic group (CO), and ethylenic linking seems to be absent in the molecule as addition-products are not easily formed. These facts led to the formula $(CH_3)_2CH{\cdot}C\langle\begin{matrix}CH_2{\cdot}CO\\CH_2{\cdot}CH_2\end{matrix}\rangle C{\cdot}CH_3$ as the most probable representation of camphor.

The oxidation of camphor with nitric acid, however, produces successively *camphoric acid*, $C_{10}H_{16}O_4$, *camphanic acid*, $C_{10}H_{16}O_5$, and *camphoronic acid*, $C_9H_{14}O_6$. Now the last of these is an open-chain compound—trimethyltricarballylic acid, $COOH{\cdot}C(CH_3)_2{\cdot}C(CH_3)(COOH){\cdot}CH_2{\cdot}COOH$. There is no isopropyl group in this compound, but, instead, two CH_3 groups attached to a C atom itself attached to two other C atoms. It is therefore probable that camphor is more correctly expressed by the formula than by that given above.

As stated on p. 557 camphene, which contains an ethylenic linking, is readily oxidised to camphor, indicating, the formula  for camphene.

Pinene and fenchene have similar constitutions.

The reactions of camphor generally produce either benzene derivatives (*e.g.* cymene) or compounds which may be regarded as derivatives of the pentamethylene ring (p. 539). *Camphoric acid* (*v.s.*) is of the latter type, being a dibasic acid, probably of the form  , the lower part of which constitutes the 5-carbon ring, there being no bond between the COOH groups. It occurs in six isomeric forms, two dextro-rotatory, two lævo-rotatory, and two inactive; the common dextro-form melts at 187° C.

Borneo camphor, $C_{10}H_{18}O$, is obtained from the exudation of the *Dryobalanops camphora*. It is neither so fusible nor so volatile as common camphor (m.-p. 203° C.; b.-p. 212° C.) and has a different odour; it also crystallises in prisms instead of octahedra. When camphor is reduced in alcoholic solution by sodium it yields Borneo camphor, and, conversely, when this is oxidised with HNO_3 it yields common camphor. Hence Borneo camphor is believed to be an alcohol, *borneol*, of similar formula to that of camphor save that $CH(OH)$ takes the place of CO. Borneol occurs in dextro-form (borneo camphor), lævo-form, and inactive form, the two latter occurring in baldrian oil (*baldrian camphor*).

Fenchone, $C_{10}H_{16}O$ (m.-p. 5° C.; b.-p. 193°C.) is a ketonic camphor, distinguished from Japan camphor by the fact that it yields meta-cymene instead of para-cymene when dehydrated. By reduction it yields *fenchyl alcohol*.

333. **Resins and Balsams.**—Resins are probably oxidation-products of essential oils, and the natural products occur dissolved in the oils as they exude from the tree, the mixture being known as an *oleoresin*. The balsams are oleoresins characterised by the presence of considerable proportions of aromatic acids.

Colophony or common *rosin* is best known among the resins, which are generally distinguished by their resinous appearance, fusibility, inflammability, burning with a smoky flame, insolubility in water, and solubility in alcohol. They are all rich in carbon and hydrogen, and contain a small proportion of oxygen; they generally have an acid character (*resin acid*), being soluble in alkalies.

Rosin melts between 100° C. and 135° C. and consists largely of *abietic acid*, $C_{19}H_{28}O_2$; it is used in making varnishes and soaps, and is destructively distilled to procure *rosin spirit* and *rosin oil*. Other resins used for varnish-making are *copal*, *sandarach*, *shellac*, *animi*, and *elemi*. To make a spirit varnish the resin is dissolved in alcohol or wood spirit (acetone), but the commoner varnish is an oil varnish made by dissolving the resin in a drying oil, like linseed oil and turpentine.

Guaicum resin is distinguished by its tendency to become blue under the influence of the more refrangible and chemically active (violet rays) of the solar spectrum, as well as under that of certain oxidising-agents, like chlorine and ozone.

Amber, a fossil resinous substance, more nearly resembles this class of bodies than any other, and contains several resinous bodies. It is distinguished by its insolubility, for alcohol dissolves only about one-eighth and ether about one-tenth.

of it. After fusion, however, it becomes soluble in alcohol, and may be used for varnishes.

Balsam of Peru, *balsam of Tolu*, and *Storax* are characterised by the presence of cinnamic acid, while *gum benzoin* is the parent substance of benzoic acid.

DERIVATIVES OF HYDROCARBONS.

334. As has been already indicated, all carbon compounds may be considered as derivatives of the hydrocarbons, containing one or more elementary atoms or compound radicles in place of hydrogen, and in every compound there is a characteristic hydrocarbon radicle, which is monovalent, divalent, or trivalent accordingly as one, two, or three hydrogen atoms have been removed from a saturated hydrocarbon in order to form it. Typical hydrocarbon radicles are $(CH_3)'$, $(C_2H_4)''$, and $(C_3H_5)'''$.

I. ALCOHOLS.

335. These compounds are comparable with the metallic hydroxides, for they contain one or more $(OH)'$ groups, and react with acids forming water and salts containing hydrocarbon radicles. Thus, the reaction $C_2H_5{\cdot}OH + H_2SO_4 = C_2H_5HSO_4 + HOH$ is comparable with the reaction $NaOH + H_2SO_4 = NaHSO_4 + HOH$. Just as a divalent or a trivalent metal forms a hydroxide containing two or three hydroxyl groups, so a divalent or trivalent radicle forms an alcohol containing two or three such groups, *e.g.*, $C_2H_4(OH)_2$, $C_3H_5(OH)_3$. Hence alcohols are classified into *monohydric*, *dihydric*, *trihydric*, &c., accordingly as they have one, two, three, &c., OH groups.

Several general methods for preparing the alcohols exist. Thus they may be formed from the halogen substitution derivatives of the corresponding hydrocarbons by treating them with moist silver oxide—$C_2H_5I + AgOH = C_2H_5OH + AgI$; from the ethereal salts (*q.v.*) by saponification—$CH_3{\cdot}COOC_2H_5$ (ethyl acetate) + $HOH = CH_3COOH + C_2H_5OH$; from hydrocarbon derivatives containing the NH_2 group by treatment with nitrous acid—$C_2H_5{\cdot}NH_2$ (ethylamine) + $NO{\cdot}OH = C_2H_5OH + N_2 + HOH$. This last reaction is typical of a widely applicable method for introducing an OH group into a compound, and is strictly comparable with the reaction between ammonia and nitrous acid at ordinary temperature (p. 106).

Alcohols have a slightly basic tendency. They easily undergo oxidation, whereby hydrogen is removed with or without the introduction of an equivalent quantity of oxygen. The products are the aldehydes (or ketones) and acids.

Monohydric alcohols of the paraffin series.—These contain OH in place of one H atom in a paraffin hydrocarbon; consequently there is an homologous series of these alcohols corresponding with the homologous series of hydrocarbons, CH_4 yielding $CH_3{\cdot}OH$, C_2H_6 yielding $C_2H_5{\cdot}OH$, C_3H_8 yielding $C_3H_7{\cdot}OH$, and so on. Thus, there is a general formula, $C_nH_{2n+1}OH$, for this series of alcohols. The substance originally called alcohol will be considered first.

Alcohol, $C_2H_5{\cdot}OH$, is systematically termed *ethyl alcohol*. It has been already stated that it can be obtained synthetically by combining C and H to form acetylene, C_2H_2, which may be converted into ethene,

C_2H_4, by nascent hydrogen; ethene can be combined with sulphuric acid to form ethyl hydrogen sulphate, $C_2H_5 \cdot HSO_4$, from which alcohol may be made by distillation with water. Or C_2H_4 may be combined with HI to obtain ethyl iodide, C_2H_5I, which, when distilled with caustic potash, yields alcohol, $C_2H_5I + KOH = C_2H_5 \cdot OH + KI$. The fact that ethyl iodide (moniodoethane), $CH_3 \cdot CH_2I$, will give alcohol in this reaction justifies the formula $CH_3 \cdot CH_2OH$ for this compound.

In nature, alcohol is found in some unripe fruits. It occurs in coal-tar, in bone-oil, and in the products of distillation of wood.

Preparation.—Alcohol is usually made by the fermention of glucose or grape-sugar brought about by *yeast*. For a laboratory experiment, two ounces (or 60 grammes) of brown sugar may be dissolved in a pint (or 500 c.c.) of water in a flask, and about a table-spoonful of brewers' yeast (or of German yeast rubbed up with water) added; in a warm room, fermentation soon begins, as indicated by the froth on the surface caused, by bubbles of CO_2. By closing the flask with a cork furnished with a tube dipping under water, the rate of fermentation may be inferred from the escaping gas. When very little more gas is disengaged (usually after about 24 hours) the flask is fitted with a tube connected with a condenser, and the liquid distilled as long as the distillate smells strongly of alcohol. The distillate is then *rectified*, or submitted to a second distillation in a smaller flask or retort, when the first portion which distils over will be much richer in alcohol. This is placed in a narrow bottle, and dried potassium carbonate, in powder, is added by degrees, with frequent shaking, as long as the liquid dissolves it. On standing, two layers are formed, the lower containing the potassium carbonate dissolved in water, and the upper containing the alcohol with about 10 per cent. of water. This upper layer is transferred to a small flask or retort, and allowed to remain for some hours in contact with powdered quick-lime to remove the water; the alcohol is then distilled off in a water-bath.

The mode of action of the yeast in causing the production of alcohol from sugar is not yet known. Yeast is a vegetable substance (*torula* or *saccharomyces cerevisiæ*) which develops from minute spores or germs carried by the air; when these come in contact with a liquid containing the nutriment necessary for the yeast plant, they multiply into a number of round or oval cells arranged in branching chains, visible under the microscope (Fig. 266). It is during this growth of the yeast that the conversion of the sugar into alcohol occurs. The pure yeast spores will not produce alcohol from pure sugar, because it does not contain the substances required to nourish the yeast; but when the spores are introduced into grape-juice, or infusion of malt (*wort*), which contain the necessary albuminous matters and phosphates, &c., they grow and cause the formation of alcohol. The crop of yeast thus raised may be used to ferment fresh portions of sugar, and is the more efficacious because, when it is removed from the surface of the liquid in which it has grown, it is accompanied by some of the nutrient materials. When yeast is added to a solution of cane-sugar ($C_{12}H_{22}O_{11}$) it causes it to become glucose, by combining with the elements of a molecule of water; $C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6$. The bulk of the glucose is then decomposed into alcohol and carbonic acid gas: $C_6H_{12}O_6 = 2C_2H_6O + 2CO_2$. About 95 per cent. of the glucose undergoes this change, and the remainder is converted into other substances, of

Fig. 266.

which the most important are glycerene, $C_3H_5(OH)_3$, (about 3 per cent.), succinic acid, $C_2H_4(CO_2H)_2$, (about 0.5 per cent.), and some of the higher members of the paraffin alcohols (fusel oil), which are always present in fermented alcoholic liquids. The liquid rises in temperature during fermentation, on account of the development of heat in the formation of carbon dioxide. The specific gravity of the solution decreases as the fermentation proceeds, because solution of alcohol is lighter than solution of sugar. A solution containing more than one-third of its weight of sugar is not fermented by yeast, and when the alcohol produced in the fermentation amounts to about one-sixth of the weight of the liquid, the growth of the yeast, and therefore the fermentation, is arrested. No fermented liquor, therefore, can contain so much as 20 per cent. of alcohol; port wine, the strongest fermented drink, contains at most 17 per cent. The yeast does not grow, and fermentation does not occur, at temperatures below 0° C. (32° F.) or above 35° C. (95° F.), 25–30° C. being most favourable. The fermentation is also arrested by strong acids, and by antiseptics such as common salt, kreasote, corrosive sublimate, sulphurous acid, and turpentine. Air is not essential to the fermentation, but favours it. In sweet wort (infusion of malt) the yeast increases to six or eight times its original weight.

Recently it has been shown that the liquid obtained by triturating yeast with sand and filtering is capable of fermenting sugar. All traces of yeast cells having been removed by the filtration it must be concluded that yeast contains an unorganised alcoholic ferment.

On the large scale, alcohol is usually made from the starch contained in potatoes, rice, and other grains. The starch, $C_6H_{10}O_5$, is converted either into glucose, by heating it with very diluted sulphuric acid (afterwards neutralised with chalk)—when it combines with a molecule of water and becomes glucose, $\cdot C_6H_{12}O_6$—or into maltose, $C_{12}H_{22}O_{11}$, by mixing it with infusion of malt; the glucose, or maltose, is fermented by yeast. The *wash*, as it is termed, is then distilled, the stills being constructed with much ingenuity, to effect the concentration of the alcohol at the least expense.

Even woody fibre, paper, linen, &c., which have the same empirical formula as starch, may be converted into glucose by the action of sulphuric acid, and may thus be made to yield alcohol. New bread, made with yeast, contains about 0.3 per cent. of alcohol, and stale bread about 0.12.

Fig. 267.

336. *Properties of alcohol.*—Characteristic odour and burning taste; sp. gr. of pure or *absolute* alcohol 0.794 at 15° C. Freezes at −112° C.; boiling-point 78°.3 C.; takes fire when a flame is brought near its surface, and burns with a pale, smokeless flame. Evaporates easily when exposed to the air, without combining with oxygen. Kept in a badly stoppered bottle, it absorbs water from the air. Alcohol may be mixed with water in all proportions, evolving a little heat, and giving a mixture rather smaller in bulk than the sum of its constituents. This may be shown by filling the vessel (Fig. 267) with water up to the neck joining the two globes, carefully filling the upper globe to the brim with (methylated) alcohol, inserting the stopper, and inverting the vessel, when the contraction of the mixture will leave a vacuum in the tube. The greatest contraction occurs when the volumes of alcohol and water are nearly equal (at 0° C., 53.9 measures of alcohol to 49.8 of water). The attraction

of alcohol for water affords one reason for its power of preserving animal and vegetable substances from putrefaction by removing the water necessary for that change.

By oxidation alcohol is converted first into aldehyde, $CH_3{\cdot}CHO$, and then into acetic acid, $CH_3{\cdot}COOH$.

Next to water, alcohol is the most valuable simple solvent. It is especially useful for dissolving resins and alkaloids which are insoluble in water. Many salts are capable of combining with alcohol, just as they do with water of crystallisation; examples of such *alcoholates*, as they are termed, are—

$$LiCl.4C_2H_6O\ ;\ CaCl_2.4C_2H_6O\ ;\ MgCl_2.6C_2H_6O\ ;\ Mg(NO_3)_2.6C_2H_6O.$$

Ethoxides or *ethylates* are compounds formed by the exchange of hydrogen in alcohol for metals; they correspond with the hydroxides, having C_2H_5 in place of H; *e.g.*, sodium ethoxide, $C_2H_5.ONa$, aluminium ethoxide, $(C_2H_5O)_6Al_2$. Sodium ethoxide is used in surgery as a caustic. Water decomposes the ethoxides, yielding alcohol and hydroxides; $C_2H_5ONa + HOH = C_2H_5OH + NaOH$.

Barium ethoxide, $(C_2H_5O)_2Ba$, is obtained by the action of anhydrous baryta on absolute alcohol. A trace of water precipitates barium hydroxide from the solution. On heating the alcoholic solution, the barium ethoxide precipitates, being less soluble in hot alcohol.

Aluminium ethoxide, $(C_2H_5O)_6Al_2$, is produced by heating aluminium in alcohol with a little iodine or stannic chloride. It melts at 135° C. and distils unchanged at 240° C. under 23mm. pressure.

Thallium ethoxide, C_2H_5OTl, is a liquid remarkable for its high specific gravity (3.68) and great refractive and dispersive action upon light.

The simplest *chemical test for alcohol* is to add to the suspected liquid hydrochloric acid and enough potassium dichromate to colour it orange-yellow, to divide it between two test-tubes for comparison, and to heat one of them till the liquid boils; if alcohol be present, the liquid will become green, and evolve the peculiar fragrant smell of aldehyde—

$$2CrO_3 + 6HCl + 3C_2H_6O = Cr_2Cl_6\ (green) + 6H_2O + 3C_2H_4O.$$

Alcohol may also be recognised by the production of acetic acid when its vapour is mixed with air and exposed to the action of platinum-black, which acts by favouring oxidation; $C_2H_6O + O_2 = C_2H_4O_2$ (*acetic acid*) $+ H_2O$. If a small beaker be wetted with alcohol and inverted over a watch-glass containing a few grains of platinum black, the liquid will soon become acid to litmus.

In contact with air and heated platinum alcohol yields much aldehyde, as well as ascetic acid (see *Lamp without flame*, p. 506).

337. The usual method of determining the strength of alcohol is to take its specific gravity by measuring a few cubic centimetres of it into a light stoppered bottle, the weight of which has been ascertained. The weight of 1 c.c. of the alcohol in grammes will be its specific gravity, very nearly. *Rectified spirit* has the sp. gr. 0.838, and contains 84 per cent. by weight of alcohol; *proof spirit* (*spiritus tenuior*) has sp. gr. 0.92, and contains only 49 per cent. by weight of alcohol; this is the weakest spirit which will answer to the old rough proof of firing gunpowder which has been moistened with it and kindled. Any spirit weaker than this leaves the powder too wet to explode, and is said to be *below proof*, whilst a stronger spirit is termed *over proof*.

A spirit of 30 per cent. (or degrees), for example, over proof, is one which requires 100 measures of it to be diluted with water to 130 measures, in order to reduce it to the strength of proof spirit. A spirit of 30 per cent. below proof contains, in every 100 measures, 70 measures of proof spirit. Some confusion occasionally arises, in commerce, from the practice of calling the percentage of *proof spirit*, in a weak spirit, the percentage of *alcohol*, which amounts to only about half the percentage of proof spirit. Ordinary alcoholic liquids must be distilled

before their alcoholic strength can be ascertained by specific gravity, on account of the presence of sugar, colouring-matter, &c.

A measured quantity of the liquid is rendered slightly alkaline with sodium carbonate, to retain volatile acids, and distilled in a flask or retort connected with a good condenser, as long as the distillate contains alcohol; usually one-third of the bulk may be distilled over for wines, and more for spirits. The volume of the distillate is then made equal to that of the liquid before distillation, by adding water, and the specific gravity is determined and compared with a Table of alcoholic strengths, which has been prepared by ascertaining the sp. gr. of alcohol of various strengths. Since the volume of the weak spirit obtained is the same as that of the original liquid, the percentage of alcohol indicated by the Table will be that present in the liquid under examination.

The weakest fermented alcoholic liquor is *porter*, which contains about 4 per cent. by weight of alcohol; the strongest is *port*, which contains about 17 per cent. Distilled spirits vary greatly in strength, 50 per cent. of alcohol being about the average, though some samples contain 70 per cent.

Methylated spirit is a mixture of 90 parts by weight of rectified spirit with 10 parts of purified wood-spirit added to it by the Excise in order to prevent its use for drinking. It may be distinguished by its odour, and by becoming red-brown with strong sulphuric acid. Since wood spirit has proved an insufficient deterrent, ½ per cent. by vol. of mineral naphtha (sp. gr. 0·8) is now also added; its presence may be recognised by the spirit becoming turbid when mixed with water.

When vapour of alcohol is passed through a red-hot tube, it is decomposed into a large number of products, among which are naphthalene, benzene, phenol, aldehyde, acetic acid, acetylene, ethene, marsh gas, carbonic oxide, and hydrogen. A mixture of one molecular weight of alcohol (46) and four molecular weights of water (72) crystallises at −34° C. When a weak spirit is cooled, ice separates until the compound $C_2H_6O.4H_2O$ is left as the unfrozen liquid, and when the temperature reaches −34° it remains constant till the whole has solidified.

338. **The principal members of the class of *monohydric alcohols* derived from the hydrocarbons of the paraffin series, at present known, are shown in the following table:**

Monohydric alcohols, $C_nH_{2n+1}\cdot OH$.

Chemical Name.	Source.*	Formula.	Boiling-point.†
1. Methyl alcohol	Distillation of wood	$CH_3\cdot OH$	66° C.
2. Ethyl „	Fermentation of sugar	$C_2H_5\cdot OH$	78° „
3. Propyl „	„ grapes	$C_3H_7\cdot OH$	97° „
4. Butyl „	„ beet	$C_4H_9\cdot OH$	117° „
5. Amyl „	„ potatoes	$C_5H_{11}\cdot OH$	137° „
6. Caproyl „	„ grapes	$C_6H_{13}\cdot OH$	157° „
7. Œnanthyl „	Distillation of castor oil with potash	$C_7H_{15}\cdot OH$	175° „
8. Capryl „	Essential oil of hog-weed	$C_8H_{17}\cdot OH$	191° „
9. Nonyl „	Nonane from petroleum	$C_9H_{19}\cdot OH$	213° „
10. Rutyl „	Oil of rue	$C_{10}H_{21}\cdot OH$	
16. Cetyl „	Spermaceti	$C_{16}H_{33}\cdot OH$	
27. Ceryl „	Chinese wax	$C_{26}H_{53}\cdot OH$	
30. Melissyl „	Bees'-wax	$C_{30}H_{61}\cdot OH$	

The usual gradation in properties attending gradation in composition among the members of homologous series, is strikingly exemplified in the alcohols. The first seven members of the series are liquid at the ordinary temperature, possess peculiar and powerful odours, and may be easily distilled unchanged. Methyl and ethyl alcohols mix in all proportions with water, but the third member,

* Of the commonest isomeride. † Of the normal alcohol (p. 567).

propyl achohol, though feebly soluble in water, is not so to an unlimited extent, while butyl alcohol is less soluble, and amyl alcohol is very sparingly soluble, in water. Caproyl alcohol, the next member, is insoluble in water, while capryl alcohol is not only insoluble, but possesses an oily character, leaving a greasy stain upon paper. The three last members in the Table are solids of a wax-like character.

Those members of the series of alcohols which may be distilled without decomposing show a nearly regular increase in the boiling-point for each addition of CH_2 in the formula; it will be seen from the Table that, excluding the difference between methyl and ethyl alcohols, the average difference in boiling-point is 19.5° C. for each CH_2 added.

339. **Methyl alcohol**, $CH_3{\cdot}OH$, is met with, in a very impure state, as *wood-spirit*, or *pyroxylic spirit*, or *pyroligneous ether*, or *wood-naphtha*. When wood is distilled, the condensed products separate into two layers, the lower of which is *wood-tar*, and the upper is a mixture of water with methyl alcohol, pyroligneous or acetic acid, $CH_3{\cdot}CO_2H$, acetone, $CH_3{\cdot}CO{\cdot}CH_3$, methyl acetate, $CH_3CO{\cdot}OCH_3$, &c. On distilling this upper layer, the portion collected below 100° C. contains these bodies; on adding chalk and re-distilling, the acetic acid is retained in the still as calcium acetate, and the distillate is sold as wood-naphtha. Its yellow colour is probably due to *pyroxanthin*, and the milkiness produced by adding water is due to certain oily substances which cause its peculiar odour. In order to obtain methyl alcohol, the wood-naphtha is distilled with quick-lime to remove water, and heated with fragments of fused calcium chloride, which dissolves in the methyl alcohol to form a crystalline compound, $CaCl_2(CH_4O)_4$. This mixture is then poured into a retort placed in a water-bath, and heated to 100° C. as long as acetone and methyl-acetate distil over. An equal weight of water is then added, which decomposes the compound with $CaCl_2$, and on continuing the distillation, methyl alcohol passes over accompanied by some water, which may be removed by contact with quick-lime and distillation.

Methyl alcohol is more easily obtained pure by boiling the wood-naphtha with anhydrous oxalic acid in a flask with a long condensing-tube, or a reversed condenser, until the methyl alcohol is converted into *methyl oxalate*, $(CO{\cdot}OCH_3)_2$, which separates in crystals on cooling. The crystals are collected on a filter, washed with water, and distilled with solution of potash; $(CO{\cdot}OCH_3)_2 + 2KOH = (CO{\cdot}OK)_2 + 2(CH_3{\cdot}OH)$. The methyl alcohol distils over with some water, which may be removed by quicklime.

Much methyl alcohol is now obtained by distilling the refuse of the beet-root sugar manufactory, and has become important as the source of many methyl-compounds employed in making dyes.

Methyl alcohol in an impure state is used as a solvent for resins in making varnishes.

Clean magnesium dissolves in absolute methyl alcohol even at ordinary temperature, evolving hydrogen and forming crystals of magnesium methoxide combined with methyl alcohol $(CH_3O)_2Mg + 3CH_3OH$.

Properties of methyl alcohol.—Much resembling ethyl alcohol, with a somewhat different odour; sp. gr. 0·7997 at 16° C., b.-p. 66° C.; m.-p. −95° C., very inflammable, burning with a pale flame. In presence of air and platinum-black, yields formic aldehyde (HCHO) and formic acid (HCO_2H); $CH_3OH + O_2 = HCO_2H + H_2O$. The formic acid may be distinguished from acetic by its property of reducing silver ammonio-nitrate to the metallic state when warmed with it. Hence, methyl and ethyl alcohols may be distinguished by distilling them with

dilute sulphuric acid and potassium dichromate, when the former yields formic and the latter acetic acid.

A suitable apparatus for distilling small quantities of liquids in making such tests is shown in Fig. 268. The condenser consists of a vessel containing cold water and surrounded by a jacket, the lower part of which terminates in a tube. The vapour entering by the side tube condenses within the jacket.

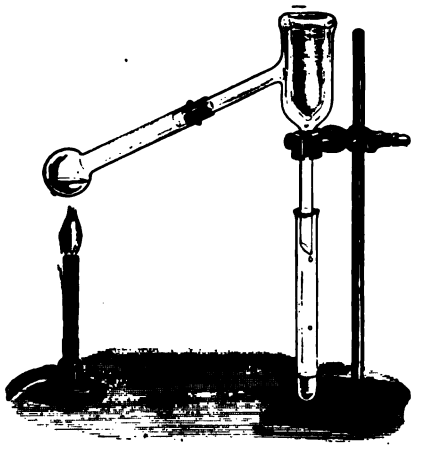


Fig. 268.

340. *Isomerism among the monohydric alcohols.* — Since methyl and ethyl alcohols are mono-substitution derivatives from methane and ethane respectively, it is not surprising that no position isomerides of these compounds are known (see p. 542). It has already been noticed that two mono-substitution derivatives of propane are possible, namely, those which have the substituent attached to the end of the three-carbon-chain, and those in which the substituent is attached to the centre carbon atom; the former kind is known as the *normal propyl* derivative, the latter as the *isopropyl* derivative. Thus, the general formula for a normal propyl derivative is $CH_3{\cdot}CH_2{\cdot}CH_2X'$, whilst that for an isopropyl derivative is $CH_3{\cdot}CHX'{\cdot}CH_3$ or $X'CH{:}(CH_3)_2$. Hence there is a normal propyl alcohol and an isopropyl alcohol.

Since butane may be regarded as methylpropane (a mono-substitution product of propane) it may be expected to exist in two modifications (p. 532). The first of these, normal butane, can yield two mono-substitution derivatives, viz., $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2X'$ and $CH_3{\cdot}CH_2{\cdot}CHX'{\cdot}CH_3$; whilst the second, secondary butane, can also yield two mono-substitution derivatives, viz., $(CH_3)_2{:}CH{\cdot}CH_2X'$ and $(CH_3)_2{:}CX'{\cdot}CH_3$. Hence there should be four butyl alcohols.

Pentane is methylbutane, but it only exists in three—instead of four—modifications (p. 519) because the methylbutanes corresponding with the second and third formulæ given above would have the same structure. By writing the formulæ for a mono-substitution-product of pentane, it will be found that eight different compounds are possible, and in many cases eight are known; eight pentyl (amyl) alcohols, for instance.

All these isomeric alcohols are divided into three classes as follows: (1) Those in which the OH group is attached to a carbon atom, which is itself attached to only one other carbon atom; these are called *primary* alcohols and contain the group $\cdot C\begin{matrix}H_2\\OH\end{matrix}$. (2) Those in which the OH group is attached to a carbon atom, which is itself attached to two other carbon atoms; these are called *secondary* alcohols, and contain the group $:C\begin{matrix}H\\OH\end{matrix}$. (3) Those in which the OH group is attached to a carbon

atom, itself attached to three other carbon atoms; these are called *tertiary* alcohols, and contain the group $:C\cdot OH$.

The following list of alcohols will furnish examples of the three classes:

Methyl alcohol	$H\cdot CH_2OH$	Primary.
Ethyl alcohol	$CH_3\cdot CH_2OH$	Primary.
Normal propyl alcohol . .	$CH_3\cdot CH_2\cdot CH_2OH$	Primary.
Isopropyl alcohol . . .	$(CH_3)_2:CHOH$	Secondary.
Normal butyl alcohol . .	$CH_3\cdot CH_2\cdot CH_2\cdot CH_2OH$	Primary.
Primary isobutyl alcohol . .	$(CH_3)_2:CH\cdot CH_2OH$	Primary.
Secondary butyl alcohol	$CH_3\cdot CH_2\diagdown\diagup CHOH$ (with CH_3)	Secondary.
Tertiary butyl alcohol . .	$(CH_3)_3:COH$	Tertiary.

Of the eight pentyl alcohols, 4 are primary, 3 secondary, and 1 tertiary.

Greater facility in naming these numerous compounds is attained by taking methyl alcohol or *carbinol* as the starting-point, and supposing the alcohols to be derived from it by substitution of alcohol radicles for the hydrogen in the methyl group. Then, the primary alcohols will be mono-substitution derivatives of carbinol, as shown in the following formulæ:

Carbinol, $CH_3\cdot OH$. Primary propyl alcohol, or *ethyl carbinol*, $CH_2(C_2H_5)\cdot OH$. Primary butyl alcohol, or *propyl carbinol*, $CH_2(C_3H_7)\cdot OH$. Primary iso-butyl alcohol, or *iso-propyl carbinol*, $CH_2(C_3H_7)\cdot OH$ (the difference here consisting in propyl. $CH_2(CH_2CH_3)$, formed by the methylation of ethyl, $CH_2(CH_3)$, and iso-propyl, $CH(CH_3)_2$, formed by the di-methylation of methyl.

The secondary alcohols may be regarded as di-substitution-products of carbinol; secondary propyl alcohol or *dimethyl carbinol*, $CH(CH_3)_2\cdot OH$, is evidently identical with iso-propyl alcohol. Secondary butyl alcohol is *ethyl methyl carbinol*, $CH(C_2H_5)(CH)_3\cdot OH$. Secondary amyl alcohol is *methyl propyl carbinol*—

$$CH(CH_3)(C_3H_7)\cdot OH.$$

Another secondary amyl alcohol is *di-ethyl carbinol*, $CH(C_2H_5)_2\cdot OH$. The tertiary alcohols would be tri-substitution-products of carbinol. Tertiary butyl alcohol is *trimethyl carbinol*, $C(CH_3)_3\cdot OH$. Tertiary pentyl alcohol is *ethyl dimethyl carbinol*. $C(C_2H_5)(CH_3)_2\cdot OH$.*

The three classes of alcohols are distinguished by their behaviour under the action of oxidising-agents, which also serves to settle their constitution. When oxidised, a primary alcohol yields an aldehyde, and ultimately an acid, containing the same number of carbon atoms as the alcohol; thus, ethyl alcohol, $CH_3\cdot C\diagup\!\!\!\diagdown^{H_2}_{OH}$, yields ethyl aldehyde, $CH_3\cdot C\diagup\!\!\!\diagdown^{O}_{H}$, and acetic acid $CH_3\cdot C\diagup\!\!\!\diagdown^{O}_{OH}$. A secondary alcohol yields a ketone containing the same number of carbon atoms; thus, secondary propyl alcohol, $(CH_3)_2:C\diagup\!\!\!\diagdown^{OH}_{H}$, yields di-methyl ketone, $(CH_3)_2:C:O$; a tertiary alcohol is either broken up into two or more acids containing less carbon, or it may yield a ketone containing one atom less carbon than itself, the atom of carbon being oxidised to carbonic or formic acid; thus, tertiary butyl alcohol, $C(CH_3)_3\cdot OH$ yields acetone, $(CH_3)_2:CO$, and formic acid, $H\cdot COOH$.

Another method for distinguishing between a primary, secondary, and tertiary alcohol is as follows: The alcohol is converted into the corresponding iodide by

* According to another system, the alcohols are named by adding *-ol* to the name of the parent hydrocarbon; thus $CH_3\cdot OH$ is *methanol*, $C_3H_7\cdot OH$ is *propanol*. Polyhydric alcohols are distinguished as *diols*, *triols*, &c.; $CH_2OH\cdot CH_2OH$ is *ethanediol*, $CH_2OH\cdot CHOH\cdot CH_2OH$ is *propanetriol*, $CH_2OH\cdot CH_2\cdot CH_2OH$ is 1:3-*propanediol*.

distilling with iodine and phosphorus (see *ethyl iodide*); the iodide is distilled with a mixture of silver nitrite with dry sand (to dilute it), when the corresponding nitro-paraffin is obtained; thus ethyl iodide yields nitro-ethane ($C_2H_5NO_2$)—

$$CH_3{\cdot}CH_2{\cdot}I + AgNO_2 = CH_3{\cdot}CH_2{\cdot}NO_2 + AgI.$$

The distillate is mixed with potassium nitrite and weak potash, and dilute sulphuric acid is gradually added; if the alcohol be primary, a *red* solution of the corresponding potassium nitrolate will be obtained, the nitro-paraffin having been converted into the corresponding *nitrolic acid* by the nitrous acid; thus, nitro-ethane yields nitrolic acid—

$$CH_3{\cdot}CH_2{\cdot}NO_2 + HNO_2 = CH_3{\cdot}C(NO_2) : NOH + H_2O.$$

Nitrolic acids are colourless, but their alkali salts have a dark red colour; they are very unstable, being decomposed into nitrous oxide and a fatty acid; thus nitrolic acid yields nitrous oxide and acetic acid. If the alcohol be secondary, a *blue* solution of a *pseudonitrol* will be obtained; thus secondary amyl alcohol, $CH(CH_3)(C_3H_7){\cdot}OH$, would yield the secondary nitro-paraffin, $CH(CH_3)(C_3H_7){\cdot}NO_2$, which would be converted by HNO_2 into the pseudonitrol, $C(NO)(CH_3)(C_3H_7){\cdot}NO_2$, giving a blue solution. If the alcohol be tertiary, no colour is produced, the tertiary nitro-paraffins being unattacked by nitrous acid.

The simplest *general method for preparing the alcohols* consists in treating the corresponding halogen substitution derivatives of the hydrocarbons with moist silver oxide, which behaves as if it were AgOH; thus, if normal butyl bromide be so treated, it yields normal butyl alcohol, $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Br + AgOH = CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2OH + AgBr$. The secondary bromide, $CH_3{\cdot}CH_2{\cdot}CH_2Br{\cdot}CH_3$, yields the secondary alcohol. The tertiary bromide yields the tertiary alcohol.

As the alcohols form the basis for the production of a large number of compounds on the small scale, their *general reactions* will be best understood when these other compounds are considered. Here it need only be mentioned that they dissolve alkali metals with evolution of hydrogen, forming the corresponding metallic *alkyloxide* or *alcoholate*, like $C_2H_5{\cdot}ONa$.

341. *Normal propyl alcohol*, or *ethyl carbinol*, $C_3H_7{\cdot}OH$, or $C_2H_5{\cdot}CH_2{\cdot}OH$, is found in the latter portions of the distillate obtained in rectifying crude spirit of wine. It smells like alcohol, has the sp. gr. 0.804, and boils at 97° C. When mixed with water it may be separated by saturating with calcium chloride, when the propyl alcohol rises to the surface, which would not be the case with ethyl alcohol. When oxidised, it yields propionic aldehyde, $C_2H_5{\cdot}CHO$, and propionic acid, $C_2H_5{\cdot}CO_2H$. *Iso-propyl* alcohol boils at 83° C., and is obtained by reducing acetone with nascent hydrogen.

The *butyl alcohol*, $C_4H_9{\cdot}OH$, originally so called, and mentioned in the table at p. 565 as obtained by the fermentation of beet-root, and also by the distillation of crude spirits, is now called *fermentation butyl alcohol*, or *primary isobutyl alcohol*, to distinguish it from the *normal butyl alcohol*, which is the real member of this homologous series of alcohols. Fermentation butyl alcohol boils at 108° C., and smells of fusel oil, which often contains it. It has sp. gr. 0.802, and is much less soluble in water than propyl alcohol is, requiring ten times its weight to dissolve it. Most salts soluble in water cause it to separate on the surface of the liquid. *Normal butyl alcohol*, or *propyl carbinol*, $C_3H_7{\cdot}CH_2{\cdot}OH$, has sp. gr. 0.810, and boils at 117° C. It is obtained by acting upon butyl aldehyde with water and sodium amalgam, to furnish nascent hydrogen, $C_3H_7{\cdot}CHO + H_2 = C_3H_7{\cdot}CH_2{\cdot}OH$.

342. The history of **amyl alcohol** resembles that of butyl alcohol, the name having been originally given to the well-known offensive and poisonous liquid called *fusel oil*, obtained in the distillation of spirits from fermented grain or potatoes. This contains, however, at least two isomeric alcohols, viz., *isobutyl carbinol*, $(CH_3)_2 : CH{\cdot}CH_2{\cdot}CH_2{\cdot}OH$ (b.-p. 131° C), and *secondary butyl* (or *methylethyl*) *carbinol*, $\begin{matrix} CH_3 \\ C_2H_5 \end{matrix}\!\!>\!CH{\cdot}CH_2OH$ (b.-p. 127° C.); this latter is optically *active*, for it contains an asymmetric carbon atom (see *stereo-isomerism*). Fusel oil has the sp. gr. 0.83, and is so sparingly soluble in water that it separates from its solution

in distilled spirits on dilution with water, rendering the liquid turbid. Its odour is very characteristic, and the vapour occasions coughing and a sensation of swelling of the head.

On writing the formulæ for the possible amyl alcohols, it will be found that 4 are primary, 3 secondary, and 1 tertiary, and that 3 of them have an asymmetric carbon atom, so that each exists in a lævo-, dextro, and inactive form making 14 amyl alcohols in all.

Tertiary amyl alcohol, *dimethylethyl carbinol*, $(CH_3)_2C_2H_5COH$, is a liquid (b.-p. 102° C) smelling of camphor, and used as a substitute for chloral as a narcotic; it is prepared from the amyl alcohol of fusel oil.

343. *Normal hexyl alcohol*, $C_5H_{11}\cdot CH_2\cdot OH$, boiling at 157° C., is not that produced by fermentation, but is obtained from the essential oil of an umbelliferous plant, *Heracleum giganteum*, which contains *hexyl butyrate*, and yields the alcohol when distilled with potash, $C_3H_7\cdot COOC_6H_{13} + KOH = C_6H_{13}\cdot OH + C_3H_7\cdot COOK$.

The *fermentation hexyl alcohol*, or *caproyl alcohol* (b.-p. 150° C.), is that obtained by distilling fermented grape-husks; it has a more unpleasant smell than the normal alcohol.

Normal capryl or *octyl alcohol*, $C_8H_{17}\cdot OH$, is obtained from the essential oil of the cow-parsnip or hog-weed (*Heracleum spondylium*), an umbelliferous plant, by distilling it with potash, which decomposes the *octyl acetate*, of which the oil chiefly consists, $CH_3\cdot COOC_8H_{17} + KOH = C_8H_{17}\cdot OH + CH_3\cdot COOK$ (*potassium acetate*). It has the sp. gr. 0.83, and boils at 199° C.

Cetyl alcohol, $C_{16}H_{33}\cdot OH$, or *ethal*, is obtained from spermaceti, found in the brain of the sperm-whale. This substance is *cetin* or *cetyl palmitate*, and when boiled for some time with potash dissolved in alcohol, it yields cetyl alcohol and potassium palmitate; $C_{15}H_{31}\cdot COOC_{16}H_{33} + KOH = C_{16}H_{33}\cdot OH + C_{15}H_{31}\cdot COOK$. On mixing the alcoholic solution with water, the cetyl alcohol is precipitated in the solid state, being insoluble in water. Cetyl alcohol is a crystalline body, fusing at 40°.5 C., and boiling at 344° C.

Ceryl alcohol, $C_{27}H_{55}\cdot OH$, is prepared from *Chinese wax*, the produce of an insect of the cochineal tribe. It consists chiefly of *cerotin* or *ceryl cerotate*, $C_{26}H_{53}\cdot COOC_{27}H_{55}$, and when fused with potash gives ceryl alcohol and potassium cerotate. By treating the fused mass with water, the cerotate is dissolved, and the ceryl alcohol is left, and may be obtained in crystals by dissolving it in ether. Its fusing-point is 79° C. It occurs in flax. Recent analyses seem to show that ceryl alcohol is $C_{26}H_{53}\cdot OH$.

Melissyl alcohol, or *myricyl alcohol*, $C_{30}H_{61}\cdot OH$, is derived from *bees'-wax*. When this is boiled with alcohol, about one-third of its weight is left undissolved: this is *myricin* or *mellissyl palmitate*, $C_{15}H_{31}\cdot COOC_{30}H_{61}$. When fused with potash it yields potassium palmitate and melissyl alcohol, which is a crystalline substance, fusing at 85° C.

344. **Monohydric Alcohols of the Olefine and Acetylene Series.**—These may be regarded as formed from the olefine and acetylene hydrocarbons in the same manner that the ordinary alcohols are derived from the paraffin hydrocarbons. They therefore correspond with the general formulæ $C_nH_{2n-1}OH$ and $C_nH_{2n-3}OH$. Those which are known are primary alcohols; thus, allyl alcohol is $CH_2 : CH\cdot CH_2OH$, derived from propylene. The alcohol from ethylene, $CH_2 : CH\cdot OH$, is a secondary alcohol (*vinyl alcohol*) and probably exists in crude ether, but it cannot be isolated because it is immediately transposed into aldehyde, $CH_3\cdot CHO$; this is in accord with other experience of the grouping : C : CHOH, which is always found to be unstable.

The alcohols of these two classes are, of course, unsaturated compounds, and readily combine with H to form the alcohols of the preceding class.

Allyl alcohol, $C_3H_5\cdot OH$, or $CH_2 : CH\cdot CH_2OH$, is obtained by heating four parts of glycerol with one part of crystallised oxalic acid in a retort at 195° C., so long as water passes over, and afterwards raising the temperature, when the allyl alcohol distils (addition of a little NH_4Cl facilitates the change). The glycerol is first converted into *monoformin*—

$CH_2OH{\cdot}CHOH{\cdot}CH_2OH + (COOH)_2 = CH_2OH{\cdot}CHOH{\cdot}CH_2(OCHO) + CO_2 + H_2O$.
The monoformin is then decomposed into allyl alcohol, CO_2 and H_2O ;

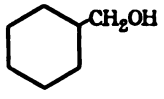
$$CH_2OH{\cdot}CHOH{\cdot}CH_2(OCHO) = CH_2 : CH{\cdot}CH_2OH + H_2O + CO_2.$$

It has a pungent smell, sp. gr. 0·87, b.-p. 96°.6 C. By very careful oxidation it yields glycerol, but when oxidised by Ag_2O it yields *acrylic aldehyde* or *acrolein*, $CH_2 : CH{\cdot}CHO$, and *acrylic acid*, $CH_2 : CH{\cdot}COOH$. This shows it to be a primary alcohol. Crude wood spirit contains a little allyl alcohol.

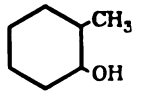
Propargyl or *propinyl alcohol*, $C_3H_3{\cdot}OH$, or $CH \vdots C{\cdot}CH_2OH$, is the alcohol corresponding with allylene. It is obtained by boiling bromallyl alcohol (itself obtained by a somewhat intricate process), $CH_2 : CBr{\cdot}CH_2OH$, with KOH ; $CH_2 : CBr{\cdot}CH_2OH + KOH = CH \vdots C{\cdot}CH_2OH + KBr + HOH$. It is a fragrant liquid of sp. gr. 0.97 and b.-p. 115° C. ; it burns with a luminous flame. Since it contains the $CH \vdots C$. group, it is capable of yielding metallic derivatives ; *cuproso-propargyl alcohol*, $CCu \vdots C : CH_2OH$ is a green precipitate.

345. **Monohydric Alcohols of the Benzene Hydrocarbons.**— It would seem at first sight as though the hydroxyl compound produced by introducing OH in the place of one of the H atoms of benzene should be an alcohol. If the structure of benzene be correctly represented by the benzene ring, however, this alcohol would partake of the nature of a tertiary alcohol, since the OH would be combined to a carbon atom itself attached by three atom-fixing powers to two other carbon atoms. As a fact, however, the hydroxy-substitution-products of the benzene hydrocarbons cannot be classed with the alcohols *when the substitution occurs in the benzene nucleus*. Such compounds as $C_6H_5(OH)$, $C_6H_4(OH)_2$, $C_6H_4(OH)(CH_3)$, differ to such an extent from the alcohols that they are classed apart as *phenols*.

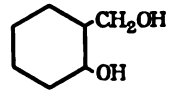
Only such hydroxy-derivatives of benzene hydrocarbons are alcohols (*aromatic alcohols*) as have *OH substituted for H in the side-chain ;* thus, whilst $C_6H_4(OH)CH_3$ is a phenol, its isomeride, $C_6H_5{\cdot}CH_2OH$, is a primary alcohol, and may be termed *benzyl alcohol* or *phenyl carbinol* (p. 568). Secondary alcohols, *e.g.*, $C_6H_5{\cdot}CHOH{\cdot}CH_3$ (from ethyl benzene), and tertiary alcohols, *e.g.*, $C_6H_5{\cdot}C(OH)\begin{matrix}CH_3\\CH_3\end{matrix}$ (from isopropyl benzene), also exist, as in the paraffin series. For every alcohol there is an isomeric phenol, and it is possible to have a *phenol-alcohol*, *e.g.*, $C_6H_4(OH){\cdot}CH_2OH$ (from hydroxytoluene), or any other substituted aromatic alcohol (Fig. 269).



Benzyl alcohol $C_6H_5\,CH_2OH$.



Orthohydroxytoluene (a phenol).



Orthohydroxybenzyl alcohol (a phenol-alcohol).

Fig. 269.

Like the paraffin alcohols, the aromatic alcohols may be prepared from the halogen substituted hydrocarbons by the action of moist silver oxide or an alkali, but the substituted halogen must, of course, be in the side-chain, *e.g.*, $C_6H_5{\cdot}CH_2Cl$ (benzyl chloride).

Benzyl alcohol, or *phenylcarbinol*, $C_6H_5{\cdot}CH_2OH$, may be obtained from *benzyl aldehyde* (*bitter-almond oil*) by the action of reducing-agents ; since benzyl aldehyde is itself capable of undergoing oxidation, it is possible to obtain both its

reduction product, benzyl alcohol, and its oxidation-product, benzoic acid, by heating it with alcoholic potash; $2C_6H_5{\cdot}CHO + KOH = C_6H_5{\cdot}CH_2OH + C_6H_5{\cdot}COOK$.

It can also be made from benzoic acid by the action of nascent H, generated by adding Na-amalgam to a boiling solution of the acid; $C_6H_5{\cdot}COOH + H_4 = C_6H_5{\cdot}CH_2OH + H_2O$. The balsams of Tolu and of Peru and storax yield benzyl alcohol when distilled with alkalies which decompose the benzyl benzoate, $C_6H_5{\cdot}COO(C_6H_5CH_2)$, and cinnamate contained in them.

Benzyl alcohol is an oily liquid heavier than water (sp. gr. 1.06), boiling at 206° C. Oxidising-agents convert it into benzaldehyde and benzoic acid, *proving it to be a primary alcohol.*

Salicyl alcohol, or *hydroxybenzyl* alcohol, $C_6H_4(OH){\cdot}CH_2OH$, shows the properties of a phenol (*q.v.*) as well as those of a primary alcohol, and is a type of the *phenol alcohols*. It is a di-substituted benzene, and therefore exists in three isomeric forms. The 1 : 2-derivative was first called *saligenin*, made from *salicin*, a crystalline substance extracted from willow-bark. This substance is a *glucoside*, and when hydrolysed (p. 265) yields glucose ($C_6H_{12}O_6$) and salicyl alcohol:

$$C_6H_4(OC_6H_{11}O_5){\cdot}CH_2OH + HOH = C_6H_{11}O_5(OH) + C_6H_4(OH){\cdot}CH_2OH.$$

1 : 2-salicyl alcohol forms tabular crystals, soluble in hot water, alcohol, and ether, fusing at 82° C. and subliming at 100° C. When oxidised it yields *salicyl aldehyde*, $C_6H_4(OH){\cdot}CHO$, and *salicylic acid*, $C_6H_4(OH){\cdot}COOH$. It gives an intense blue colour with ferric chloride (*cf. Phenols*).

Cinnamyl alcohol is the primary alcohol corresponding with the unsaturated hydrocarbon cinnamene (p. 550); its formula is $C_6H_5{\cdot}CH : CH{\cdot}CH_2OH$, *phenyl allyl alcohol*. It also is obtained from *storax*, a fragrant balsam exuded by the *Styrax officinale*, a tree found in Syria and Arabia, sometimes used as a pectoral remedy. When this is digested for some hours with a weak solution of soda, and the residue extracted with a mixture of ether and alcohol, needle-like crystals of *styracin* are obtained. This substance is *cinnamyl cinnamate*, $C_6H_5{\cdot}CH : CH{\cdot}COO(C_6H_5{\cdot}CH : CH{\cdot}CH_2)$, and yields cinnamyl alcohol and potassium cinnamate when distilled with KOH; $C_9H_9{\cdot}C_9H_7O_2 + KOH = C_9H_9{\cdot}OH + KC_9H_7O_2$.

The alcohol smells of hyacinths, melts at 33° C. and boils at 250°. It dissolves sparingly in water, but easily in alcohol or ether. When oxidised it yields *cinnamic aldehyde* and *cinnamic acid*.

Alcohols of the hydrocarbons containing more than one benzene nucleus are of minor importance. *Diphenylcarbinol* (*benzhydrol*), $(C_6H_5)_2CH.OH$, is a secondary alcohol obtained by reducing benzophenone (*q.v.*); it melts at 68° C.

Triphenylcarbinol, $(C_6H_5)_3C.OH$, is a tertiary alcohol, important from its relation to the "aniline dyes." It is formed by oxidising triphenylmethane (p. 551) with chromic acid in glacial acetic acid, melts at 159° and boils at 360° C.

Naphthalene and anthracene alcohols also exist.

346. **Thio-alcohols** or **mercaptans** are analogous to the alcohols, but contain S in place of O, and as the latter are hydroxides of the alcohol radicles, so the thio-alcohols (R·SH) are the hydrosulphides. The *thio-ethers*, R_2S, or sulphides of the alcohol radicles, may also be considered here: they are the analogues of the ethers, R_2O.

Mercaptan, $C_2H_5{\cdot}SH$, was named from its remarkable action on mercury compounds (*mercurio aptum*). It is made (for making sulphonal) by distilling KSH with C_2H_5Cl in alcoholic solution, or, on a smaller scale, with calcium sulphethylate (*q.v.*):—$Ca(C_2H_5SO_4)_2 + 2KSH = CaSO_4 + K_2SO_4 + 2(C_2H_5{\cdot}SH)$.

A solution of KSH is made by saturating potash of sp. gr. 1.3 with H_2S, and this is distilled, in a salt-and-water bath, with an equal volume of solution of calcium sulphethylate of sp. gr. 1.3. The mercaptan forms the upper layer of the distillate, and is characterised by its powerful smell of garlic. It is a volatile liquid, of sp. gr. 0.835, and boils at 36° C. A drop exposed to the air is frozen to a crystalline mass by its own evaporation. It burns with a blue flame. Mercaptan is sparingly soluble in water, but dissolves in alcohol and ether. It is unaffected by caustic alkalies, but alkali metals act on it as in the case of alcohol, displacing hydrogen and forming *mercaptides*, *e.g.*, $C_2H_5{\cdot}SK$, which are crystalline bodies soluble in water.

Mercuric oxide evolves much heat with mercaptan, forming a white crystalline inodorous compound; $HgO + 2(C_2H_5{\cdot}SH) = H_2O + (C_2H_5S)_2Hg$ (*mercuric mercaptide*). This is insoluble in water, but may be crystallised from alcohol, or from strong HCl. Potash does not decompose it. H_2S converts the mercury into sulphide and reproduces mercaptan. Mercaptides (*thio-ethoxides*) of other

metals may be precipitated by metallic salts from an alcoholic solution of mercaptan.

By distilling mercuric thio-ethylate, *di-ethyl sulphide* or *thio-ether*, $C_2H_5{\cdot}S{\cdot}C_2H_5$, may be obtained; $(C_2H_5S)_2Hg=(C_2H_5)_2S+HgS$. This may also be prepared by distilling potassium sulphethylate with potassium sulphide; $2KC_2H_5SO_4+K_2S=2K_2SO_4+(C_2H_5)_2S$. It resembles mercaptan, but boils at 91° C. Its alcoholic solution gives, with mercuric chloride, a white crystalline precipitate of $(C_2H_5)_2S{\cdot}HgCl_2$.

Allyl sulphide, $(C_3H_5)_2S$, is the main constituent of *essential oil of garlic*, and occurs in several cruciferous plants. It boils at 140° C., dissolves sparingly in water, and behaves like ethyl sulphide.

Ethyl disulphide, $(C_2H_5)_2S_2$, is obtained when potassium disulphide and sulphethylate are distilled. It may also be formed by heating mercaptan to 150° C. with sulphur; $2(C_2H_5SH)+S_2=(C_2H_5)_2S_2+H_2S$; or by decomposing sodium mercaptide with iodine; $2(C_2H_5SNa)+I_2=2NaI+(C_2H_5)_2S_2$. It is an alliaceous liquid, boiling at 151° C. *Ethyl sulphoxide*, $(C_2H_5)_2OS$, is a syrupy liquid resulting from the action of dilute nitric acid on ethyl sulphide.

Ethyl sulphone, $(C_2H_5)_2SO_2$, is a very stable crystalline body formed when ethyl sulphide is oxidised by strong nitric acid; it fuses at 70° C. and boils at 248° C., but sublimes at 100° C. It is soluble in water and alcohol.

When ethyl sulphide and ethyl iodide are heated together with a little water for some hours in a flask with an inverted condenser, the mixture, on cooling, deposits colourless prisms of *tri-ethyl-sulphine iodide*, $(C_2H_5)_3S{\cdot}I$, which are soluble in water and alcohol, but insoluble in ether. This compound is remarkable for producing a series of compounds in which the iodine may be exchanged for other chlorous radicles, giving rise to *tri-ethyl-sulphine salts*, in which the S is quadrivalent; thus, in the iodide, it is attached to four monad radicles, viz., $(C_2H_5)_3$ and I. By decomposing the iodide with silver hydroxide, the *tri-ethyl-sulphine hydroxide*, $(C_2H_5)_3S{\cdot}OH$, is obtained; it is a deliquescent crystalline body possessing the properties of a powerful caustic alkali.

Compounds similar to the foregoing have been obtained from the alcohols formed by the other radicles of this series.

347. **Dihydric Alcohols, or Glycols.**—The dihydric alcohols may be regarded as derived from the saturated hydrocarbons by the substitution of hydroxyl groups for two H atoms; equally well, they may be said to be olefine hydrocarbons which have combined with two hydroxyl groups, and this is the view expressed by their nomenclature; ethylene glycol, $C_2H_4(OH)_2$, and propylene glycol, $C_3H_6(OH)_2$, are examples. Like the monohydric alcohols, a general method for their preparation consists in the treatment of the corresponding bromo-derivatives with alkalies, or, what is equivalent, an alkali carbonate, or lead hydroxide, and water.

The simplest glycol would be $CH_2(OH)_2$, from methane; but this has never been isolated, and it appears to be a fact that *no compound can exist which has two hydroxyl groups attached to one carbon atom* (*cf.* the non-existence of carbonic acid, $OC(OH)_2$; p. 127). There is evidence to show that in all the glycols the OH groups are attached to different carbon atoms. For example, ethylene glycol is $CH_2OH{\cdot}CH_2OH$, not $CH_3{\cdot}CH(OH)_2$, and cannot exist in isomeric forms; *propylene glycol* may be either $CH_2OH{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, or $CH_3{\cdot}CHOH{\cdot}CH_2OH$, the former of which contains two primary alcohol groups, and may be termed a *diprimary* glycol, whilst the latter is a *secondary-primary* glycol.* Since *disecondary*, *ditertiary*, *secondary-tertiary* and *primary-tertiary* glycols

* The glycols are either α-, β-, or γ-, &c., glycols accordingly as the OH groups are attached to the 1:2, 1:3, 1:4, &c., C atoms of the chain, respectively; thus—

$$CH_2OH{\cdot}CH_2{\cdot}CH_2OH$$

is β-propylene glycol, the α-isomeride being $CH_3{\cdot}CHOH{\cdot}CH_2OH$.

are also possible, the cases of isomerism among the glycols are very numerous.

The OH groups in the glycols are capable of the same transformations as is the OH in a monohydric alcohol; the H in them can be exchanged for alkali metals; the hydroxyl groups can be exchanged for acid radicles, &c. Two series of such substituted glycols exist, those in which both OH groups have undergone the change, and those in which only one has been altered; thus, $CH_2ONa{\cdot}CH_2OH$ and $CH_2ONa{\cdot}CH_2ONa$; $CH_2Cl{\cdot}CH_2OH$ and $CH_2Cl{\cdot}CH_2Cl$.

The oxidation of the glycols yields the same kind of products as those from the oxidation of the alcohols; but since there are two alcoholic groups to be oxidised, a very large number of products is obtainable; for example, the two primary alcohol groups in $CH_2OH{\cdot}CH_2OH$ can both be oxidised to aldehyde groups, $CHO{\cdot}CHO$, or to acid groups, $COOH{\cdot}COOH$; or only one of them may be so oxidised, yielding *alcohol-aldehydes*, $CHO{\cdot}CH_2OH$, or *alcohol acids*, $COOH{\cdot}CH_2OH$; *aldehyde-acids*, $CHO{\cdot}COOH$, will also be possible. If the glycol contain a secondary alcohol group (:CHOH), *ketone-alcohols*, *ketone-aldehydes*, *ketone-acids*, and *diketones* may also be prepared. Hence the glycols give rise to a very large number of derivatives, many of which are very important, although the same cannot be said of the glycols themselves.

The dialcohols, alcohol-aldehydes, alcohol-acids, and alcohol-ketones, containing the group CH_2OH, are frequently termed *hydroxy-* or *oxy-* derivatives of the corresponding paraffin compounds. Thus $CH_2OH{\cdot}CH_2OH$ may be regarded as *hydroxyethyl alcohol* (*oxyethyl alcohol*), *i.e.*, ethyl alcohol, in which H has been exchanged for OH; $CH_2OH{\cdot}CHO$ as hydroxyacetic aldehyde, and $CH_2OH{\cdot}COOH$ as hydroxyacetic acid.

The glycols are somewhat viscid, neutral liquids. The increase in the number of OH groups in an alcohol seems to tend to increase the boiling point, the viscidity and the solubility in water; solubility in alcohol and ether decreases. The glycols have a sweetish taste, a property much enhanced in glycerol and the sugars.

Glycol, $CH_2OH{\cdot}CH_2OH$, or *ethylene glycol*, is a much more artificial product than alcohol, having been discovered as lately as 1856. It is prepared by decomposing ethylene bromide with potassium carbonate. Ethylene (p. 535) is first converted into *ethylene bromide* by passing it slowly into 50 grams of bromine under water, well cooled, until the bromine is bleached, or nearly so. The heavy layer of ethylene bromide is shaken with a little weak potash, the upper watery layer drawn off, and 50 grams of the bromide heated with 40 of potassium carbonate, and 100 of water, for eighteen hours, in a flask provided with a reversed condenser (Fig. 270); when the bromide no longer condenses and runs back, the condenser is placed in its proper position and the contents of the flask distilled. After all the water has passed over, the flask is strongly heated by a large Bunsen burner, when the glycol distils. The reaction is expressed by the equation $C_2H_4Br_2 + K_2CO_3 + H_2O = C_2H_4(OH)_2 + 2KBr + CO_2$, which exemplifies the tendency of alkaline reagents, in the presence of water, to effect the substitution of hydroxyl for halogens.

Glycol is a colourless liquid, less mobile than alcohol, and almost inodorous. It has a sweet taste, sp. gr. 1.125 at 0°, and the high boiling-point 197° C. Its vapour is inflammable, but will not take fire at common temperatures like alcohol. Glycol mixes with water and alcohol in all proportions, but ether does not dissolve it.

Sodium dissolves in glycol, as in alcohol, evolving hydrogen, and yielding *monosodium glycol*, $CH_2OH{\cdot}CH_2ONa$, corresponding with sodium ethoxide, $C_2H_5{\cdot}ONa$. On heating this with more sodium, a second atom of H is displaced

yielding *disodium glycol*, $C_2H_4(ONa)_2$. Water converts both compounds into glycol and sodium hydroxide.

Glycol chlorhydrin is glycol in which Cl has been substituted for one hydroxol group; $CH_2OH{\cdot}CH_2Cl$; and is prepared by saturating glycol with HCl, and heating in a sealed tube to 100° C.; $C_2H_4(OH)_2 + HCl = C_2H_4{\cdot}OH{\cdot}Cl + HOH$. It has also been obtained by the combination of ethylene, C_2H_4, with hypochlorous acid, ClOH. It permits the conversion of a dihydric into a monohydric alcohol, for it yields ethyl alcohol when acted on by (the nascent hydrogen from) water and sodium-amalgam; $C_2H_4{\cdot}OH{\cdot}Cl + 2H = C_2H_5{\cdot}OH + HCl$. When oxidised it yields monochloracetic acid, $CH_2Cl{\cdot}COOH$, in which it is obvious that the Cl cannot be attached to the same carbon atom as that to which the O and OH are attached (or the substance would not be an acid); this proves that glycol chlorhydrin must contain Cl and OH attached to different carbon atoms, and settles the *constitution of glycol.*

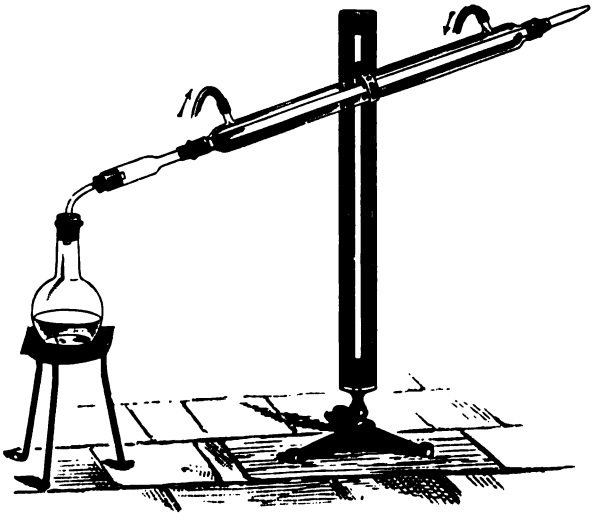


Fig. 270.—Reversed condenser.

The first stage in the oxidation of glycol is the formation of *glycol dialdehyde*, or *glyoxal;* the relation of this body to glycol is shown thus: glycol, $CH_2OH{\cdot}CH_2OH$; glyoxal, $CHO{\cdot}CHO$.

The further oxidation of glycol yields two acids, glycollic acid, $COOH{\cdot}CH_2OH$, and oxalic acid, $COOH{\cdot}COOH$.

The glycols from the hydrocarbons containing one or more benzene nuclei, have the hydroxyl groups in the side-chains; they have been little studied.

Hydrobenzoin, $(C_6H_5)CHOH : CHOH(C_6H_5)$, *toluylene-glycol*, is derived from stilbene (p. 551); it crystallises in plates, and melts at 134° C. An isomeride, *isohydrobenzoin*, melts at 119° C. and occurs in two optically active and one inactive forms; both isomerides are produced when benzaldehyde (*q.v.*) is reduced with nascent hydrogen.

The **pinacones** are di-tertiary glycols, obtained, together with secondary alcohols, by the action of nascent hydrogen on the ketones. Thus, acetone undergoes a condensation according to the equation, $2(CH_3)_2CO + H_2 = (CH_3)_2(HO)C{\cdot}C(OH)(CH_3)_2$, *dimethyl pinacone.*

348. **Trihydric Alcohols, or Glycerols.**—These may be regarded as derived from saturated hydrocarbons, by substituting three OH groups for three H atoms. Since two OH groups cannot remain combined with one carbon atom (p. 573), there can be no glycerol which contains

fewer than three carbon atoms; thus, $C_3H_5(OH)_3$ must be the first member of the series. The radicles of the glycerols may obviously be regarded as trivalent radicles—*e.g.* $(C_3H_5)'''$, *glyceryl* or *propenyl*. Comparatively few of the glycerols are known; what was said with regard to isomerism, substitution derivatives, and oxidation products of the glycols, applies with even more cogency to glycerols, where there are three hydroxyl groups to be substituted and three alcoholic groups to be oxidised. It will be noted, however, that a glycerol formed from an open-chain saturated normal hydrocarbon must always contain at least one secondary alcoholic group.

Glycerine, or *Glycerol*, $C_3H_5(OH)_3$, or $CH_2OH{\cdot}CHOH{\cdot}CH_2OH$, was formerly termed the sweet principle of fats, on account of the facility with which it may be prepared from most of the natural fats, which are thence called *glycerides*. Glycerine is also formed during the alcoholic fermentation of sugar, and is present in small quantity in beer and wine.

Preparation of glycerine.—Glycerine is contained in the refuse liquor (*spent lyes*) of the soap-maker, being always produced when oils and fats are saponified by alkalies, and remaining in solution when the soap is separated by adding salt. The chemistry of the saponification of oils and fats will be considered under the head of *ethereal salts*, to which class these bodies belong. The soap lyes are concentrated until most of the salt has crystallised and most of the water evaporated. The crude glycerine thus obtained is distilled under diminished pressure in a current of superheated steam, when water passes over first and is followed by glycerine, the temperature of the receiver being high enough to prevent much of the superheated steam from condensing. The more or less dilute glycerine thus obtained is concentrated in a vacuum pan.

Only within recent years have methods of evaporation been so far improved that it has paid the soap-maker to recover glycerine from his lyes. The candle-maker used to be the sole producer. In this industry palm-oil is decomposed by superheated steam to obtain palmitic acid for making candles. The operation is conducted in a still, and the distillate consists of a layer of palmitic acid floating on an aqueous solution of glycerine. The latter is drawn off and concentrated as described above, the process being simplified by the absence of salt. The palmitic acid solidifies to a white crystalline substance.

Previously to 1850, glycerine was made only on a laboratory scale by the process discovered by Scheele in 1779, which consisted in boiling olive oil with lead oxide (litharge, PbO) and water, when *lead oleate*, or *lead plaster*, remained, while the glycerine dissolved in the water from which it was obtained by evaporation, after precipitating the dissolved lead by H_2S.

Glycerine has been made artificially from propylene by combining it with chlorine to form *propylene chloride*, $CH_2Cl{\cdot}CHCl{\cdot}CH_3$, which is heated with iodine chloride to convert it into *propenyl tri-iodide*, $CH_2I{\cdot}CHI{\cdot}CH_2I$; by heating this in a sealed tube, with much water, at 160° C., it is converted into glycerine; $C_3H_5I_3 + 3HOH = C_3H_5(OH)_3 + 3HI$. This synthesis, together with the fact that glycerine can be made by oxidising allyl alcohol, $CH_2 : CH{\cdot}CH_2OH$, establishes the *constitution of glycerol*, if it be admitted that one carbon atom cannot hold two OH groups.

Properties of glycerine.—Resembles syrup in taste and consistence; sp. gr. 1.269 at 12° C.; boils at 290° C., but then undergoes partial decomposition. At 12 mm. pressure it boils at 170° C. It is slightly

volatile at 100° C., but not at the ordinary temperature. If kept at 0° C. for some time, a strong aqueous solution of glycerine deposits crystals, especially if a ready-made crystal be introduced; pure glycerine solidifies at − 40° C. to a gummy mass, which melts at 17° C. It does not inflame until heated to 150° C., when it burns with a flame resembling that of alcohol. It absorbs water easily from the air, and dissolves without limit in water and alcohol, but is insoluble in ether.

On account of its never drying, glycerine is useful in many cases when it is desired to keep any substance moist and supple. Water mixed with an equal weight of glycerine is sometimes used in gas-meters, being much less easily frozen than water, and less liable to dry up. Glycerine is used in pharmacy, but its chief application is in making nitroglycerine (*q.v.*).

Glycerine possesses extensive solvent powers, like alcohol, dissolving most substances which are soluble in water, and some others, such as metallic oxides, which are insoluble in water.

A characteristic property of glycerine is that of yielding an exceedingly pungent and irritating substance, known as *acrolein*, or *acrylic aldehyde*, $C_2H_3{\cdot}CHO$, when sharply heated, or subjected to the action of dehydrating agents, $C_3H_5(OH)_3 = C_2H_3{\cdot}CHO + 2H_2O$. The best test for identifying glycerine is to mix it with powdered $KHSO_4$ and heat it strongly, when the intolerable odour of acrolein is perceived. It is this substance which causes the offensive smell of smouldering candles made of tallow and other glycerides.

By treatment with a mixture of nitric and sulphuric acids glycerine is converted into *nitroglycerine* or *glyceryl trinitrate*, $C_3H_5(NO_3)_3$, a powerfully explosive compound which will be described in the section on *ethereal salts*.

As glycerol contains two primary alcohol groups, CH_2OH, which are known to be oxidisable first to aldehyde groups, CHO, and then to acid groups, COOH, and also a secondary alcohol group, which is oxidisable to a ketone group, CO, no fewer than 11 oxidation-products of glycerol are theoretically possible. Only six, however, are at present known, namely: glyceric aldehyde, $CHO{\cdot}CHOH{\cdot}CH_2OH$: dihydroxyacetone, $CH_2OH{\cdot}CO{\cdot}CH_2OH$; glyceric acid, $COOH{\cdot}CHOH{\cdot}CH_2OH$: tartronic acid, $COOH{\cdot}CHOH{\cdot}COOH$; mesoxalic acid, $COOH{\cdot}C(OH)_2{\cdot}COOH$; and hydroxypyroracemic acid, $CH_2OH{\cdot}CO{\cdot}COOH$. Except the last named, all these are obtainable by the direct oxidation of glycerol. When H_2O_2 (in presence of a small quantity of a ferrous salt) is the oxidant, a mixture of glyceric aldehyde and dihydroxyacetone is formed which was originally supposed to be a single compound and was called "glycerose." Dilute nitric acid produces glyceric and tartronic acids, while oxidation with bismuth nitrate and nitre forms mesoxalic acid. More energetic oxidising-agents yield glycollic acid, $CH_2OH{\cdot}COOH$; oxalic acid, $COOH{\cdot}COOH$; and glyoxylic acid, $CHO{\cdot}COOH$.

When reduced with hydriodic acid glycerol yields allyl iodide, $CH_2 : CH{\cdot}CH_2I$; isopropyl iodide, $CH_3{\cdot}CHI{\cdot}CH_3$; and propylene, $CH_3{\cdot}CH : CH_2$.

Two compounds corresponding with the ethoxides may be obtained by the action of sodium ethoxide on glycerol in alcohol, *sodium propenoxide*, $C_3H_5(OH)_2ONa$, and *disodium propenoxide*, $C_3H_5OH(ONa)_2$.

By treating α-chlorhydrin (*q.v.*), with BaO, HCl is abstracted and *glycide alcohol* is obtained: $\begin{matrix}Cl{\cdot}CH_2\\ |\\ HOC{\cdot}CH_2OH\end{matrix} - HCl = O\begin{matrix}CH_2\\ \diagup\\ \diagdown\\ CH_2OH\end{matrix}$; this is a colourless liquid, boiling with decomposition at 162° C. It combines with water to form glycerol.

349. **Tetrahydric and Higher Polyhydric Alcohols.**—Alcohols containing 4, 5, 6, 7, 8, and 9 hydroxyl groups are known. The number of hydroxyl groups present in an alcohol is ascertained by heating the

alcohol with acetic anhydride, $(CH_3CO)_2O$, and sodium acetate, when as many acetic acid radicles (acetyl, CH_3CO) enter into the composition of the alcohol, as there are hydroxyl groups in the alcohol; for example, the compound called *erythrite* is known to be a tetrahydric alcohol, because it forms an acetate containing four acetyl groups;

$$C_4H_6(OH)_4 + 4(CH_3CO)_2O = C_4H_6(OCH_3CO)_4 + 4CH_3COOH.$$

The lowest member of each series of polyhydric alcohols must have at least as many carbon atoms as it has OH groups, otherwise one carbon atom would have to hold two hydroxyl groups, and the compound would break up (p. 573). The derivatives and oxidation-products of these alcohols are similar in constitution to those of glycol.

Most of the higher alcohols that are known are obtained from natural sources; they are many of them sweet, and some were for long classed with the sugars, with which, indeed, they are closely connected.

Erythrite. *erythritol*, or *phycite*, $C_4H_6(OH)_4$, or $CH_2OH{\cdot}[CHOH]_2{\cdot}CH_2OH$, is obtained from certain lichens, such as the *Roccella tinctoria*, or *Orchella weed*, by boiling with milk of lime, filtering, precipitating the excess of lime by CO_2, evaporating the filtrate to a small bulk, and treating with alcohol, when erythrite crystallises in prisms, which fuse at 126° C. and sublime at 300°, though not quite undecomposed. It is easily soluble in water, and has a sweet taste; sparingly soluble in cold alcohol, and insoluble in ether.

In several of its reactions erythrite resembles glycerine. When it is dissolved in nitric acid, and sulphuric acid added, it yields a crystalline precipitate of *nitro-erythrite*, $C_4H_6(NO_3)_4$, which is explosive like nitroglycerine.

If, in the treatment of the lichen, cold milk of lime be used, the filtrate, when saturated with CO_2, gives a mixed precipitate of calcium carbonate and *erythrin*, which may be extracted by alcohol, and crystallised. Erythrin is *erythrite di-orsellinate*, $C_4H_6(OH)_2(OC_8H_7O_3)_2$, and belongs to the class of ethereal salts. It appears to exist as such in the lichen, and is decomposed into erythrite and calcium orsellinate when boiled with calcium hydroxide. Erythrite exists ready formed in certain *algæ*, notably in *Protococcus rulgaris*. This natural erythrite is optically inactive. Both it and another inactive form (believed to be internally compensated —see p. 621) may be synthetised from divinyl $CH_2 : CH{\cdot}CH : CH_2$ by adding Br to form two dibromides, which are stereoisomerides and can be oxidised by permanganate to corresponding bromhydrins $CH_2Br[CHOH]_2CH_2Br$: these yield the natural erythrite and its isomeride (m. p. 72° C.) when treated with KOH and water. A dextro- and a lævo-erythritol have also been obtained.

Arabite, or *arabitol*, $CH_2OH{\cdot}[CHOH]_3{\cdot}CH_2OH$, is obtained by reducing *arabinose* (*q.v.*) with nascent hydrogen. It melts at 102° C.

Mannite, or *mannitol*, $CH_2OH{\cdot}[CHOH]_4{\cdot}CH_2OH$, a hexahydric alcohol, is a sweet substance contained in *manna*, from which it may be extracted by boiling with alcohol, when it crystallises, on cooling, in fine needles, fusing at 166° C. It is rather sparingly soluble in cold water and alcohol, but easily on heating, and is insoluble in ether. When oxidised in presence of platinum black, it yields the sugar mannose, $C_6H_{12}O_6$ (*q.v.*), and when this is further oxidised it becomes *mannonic acid*, $CH_2OH{\cdot}[CHOH]_4{\cdot}CO_2H$. The natural mannite is dextro-rotatory; a lævo- and an inactive form are also known, as will be explained later.

By treatment with nitric acid, mannite is converted into an explosive crystalline body, which is *nitromannite*, or *mannyl hexanitrate*, $C_6H_8(NO_3)_6$, re-converted into mannitol by $(NH_4)_2S$. When treated with HI, mannite becomes secondary hexyl iodide,

$$CH_2OH{\cdot}CHOH{\cdot}CHOH{\cdot}CHOH{\cdot}CHOH{\cdot}CH_2OH + 11\,HI = CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CHI{\cdot}CH_3 + 6HOH + I_{10}.$$

Mannite is found among the products of the *viscous fermentation* of saccharine liquors, when they are said to become *ropy*; beet-root juice is especially liable to this change.

Mannite is an important substance in vegetable chemistry, since it occurs not only in manna, the dried exudation of the *Ornus*, or manna ash, growing in the South of Europe, but also in the sap of the common ash (*Fraxinus excelsior*), of the larch, apple, cherry, and lime: in the leaves of the syringa and privet; in the bulbs of *Cyclamen europæum* (sow-bread), in the bark of the wild cinnamon, in some lichens, seaweeds, sugar-cane, mushrooms, celery, asparagus, olives, and onions. The seaweed *Laminaria saccharina*, or *sugar-wrack*, contains 12 per cent. of mannite, which is sometimes found as an efflorescence on the surface of the weed. It has also been found in the root of the monkshood (*Aconitum napellus*). The *Agaricus integer*, a common fungus, contains when dry about 20 per cent. of mannite.

Mannitane, $C_6H_8(OH)_4O$, is prepared by heating mannite to 200° C.; $C_6H_8(OH)_6 = C_6H_8(OH)_4O + H_2O$. It is a viscous substance very similar to glycerol, and forming compounds when heated with the fatty acids which closely resemble the glycerides, and are saponified by alkalies in the same way.

Dulcite, or *dulcitol*, is isomeric with mannite, and much resembles it. It is extracted from Madagascar manna by boiling water. It is nearly twice as soluble in water as mannite is, but much less soluble in alcohol. It melts at 188° C.

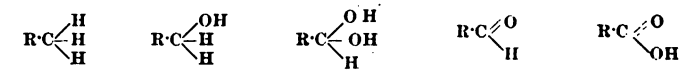
Sorbitol, $C_6H_8(OH)_6$, another isomeride of mannite, is found in the berries of the mountain ash (*Sorbus aucuparia*). It is more fusible (110° C.) than the others.

II. ALDEHYDES.

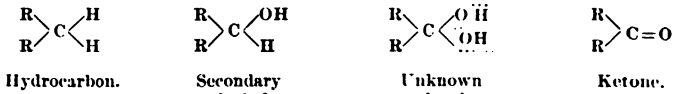
350. These compounds are the first products of the oxidation of all alcohols containing the primary alcoholic group $\cdot C\overset{H_2}{\diagdown OH}$, which becomes $\cdot C\overset{H}{\diagdown O} + HOH$. They differ from the parent alcohols by two atoms of hydrogen; thus, ethyl alcohol, $CH_3 \cdot CH_2OH$, yields acetic aldehyde, $CH_3 \cdot CHO$, and so on, there being one or more aldehydes corresponding with each of the alcohols already described. They readily pass by oxidation into the corresponding acids, the group $\cdot C\overset{O}{\diagdown H}$ becoming $\cdot C\overset{O}{\diagdown OH}$, and are named after the acids into which they are converted. Since the oxidation of primary alcohols to aldehydes consists merely in the removal of H_2 (whence the name—*al*[*cohol*] *dehyd*[*rogenatum*]), and since the aldehyde in all its reactions appears still to contain the hydrocarbon radicle which was contained in the alcohol, the above view of the constitution of these compounds may be presumed to be correct. It is supported by the fact that when an aldehyde reacts with PCl_5 the oxygen atom is exchanged for *two* chlorine atoms, $CH_3 \cdot CHO + PCl_5 = CH_3 \cdot CHCl_2 + POCl_3$, showing that the aldehyde cannot contain the O in the form of OH. For *when a compound containing OH reacts with PCl_5, the OH is exchanged for Cl and HCl is a product of the reaction*, e.g., $CH_3 \cdot CH_2OH + PCl_5 = CH_3 \cdot CH_2Cl + POCl_3 + HCl$. Position isomerism can only occur in the radicle of the aldehyde; thus, in the general formula, R·CHO, R may occur in isomeric forms, but there are no secondary and tertiary aldehydes in the sense that there are secondary and tertiary alcohols.

As already stated (p. 573), glycols of the type $R \cdot CH(OH)_2$ do not exist, although many compounds are known which might be expected to yield them under appropriate treatment; for instance, by analogy with the reaction between ethyl chloride and moist silver oxide, that

between this oxide and *ethylidene chloride*, $CH_3 \cdot CHCl_2$, might be expected to yield ethylidene glycol $CH_3 \cdot CH(OH)_2$, but as a fact yields aldehyde and water, $CH_3 \cdot CH(OH)_2$, becoming $CH_3 \cdot CHO + HOH$. Thus the aldehydes may be regarded as the anhydrides of these unknown glycols, and it may be supposed that the latter are the true products of oxidation of the primary alcohols, being formed by the substitution of OH for a second H atom in the parent hydrocarbon; the glycol thus formed, however, at once passes into its anhydride, the aldehyde. This view of the process of oxidation is supported by the oxidation of the aldehyde to the acid, consisting of the substitution of OH for H. The following formulæ make these remarks clear, but it must be remembered that the alcohol is not formed by oxidation of the hydrocarbon:



Hydrocarbon. | Primary alcohol. | Unknown glycol. | Aldehyde. | Acid.

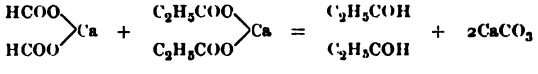


Hydrocarbon. | Secondary alcohol. | Unknown glycol. | Ketone.

The aldehydes are unsaturated in the sense that the oxygen atom is doubly linked to carbon, and they show a tendency to combine as a whole with other compounds, the aldehyde group $\cdot CH=O$ becoming $\cdot CH\langle^{O-}_{\ }$. This tendency leads to the formation of derivatives of the aforesaid unknown glycols and to a number of nucleal condensations (p. 531), which render the aldehydes useful in building up new carbon nuclei. The chief reactions of this kind will be noticed in the description of acetic aldehyde, the behaviour of which is identical with that of the majority of aldehydes.

The readiness with which the aldehydes undergo oxidation to the corresponding acids makes them powerful reducing-agents.

351. **Aldehydes from the Paraffin Alcohols.**—The oxidation of the primary alcohols is not the only general reaction for preparing the aldehydes of this series. They may be obtained by distilling a dry mixture of calcium formate and the calcium salt of the acid corresponding with the adlehyde required.



Calcium formate. | Calcium propionate. | Propionic aldehyde.

Formic aldehyde, *formaldehyde*, or *methyl aldehyde*, $H \cdot CHO$, is a gas and boils at -21° C. It is formed when a mixture of methyl alcohol vapour and air is passed over a red-hot platinum wire, $CH_3 \cdot OH + O = H \cdot CHO + HOH$. It is now made on a large scale by a secret process and sold in aqueous solution containing 40 per cent. under the name of *formaline* for use as an antiseptic and in the manufacture of dye-stuffs;

the solution has a suffocating odour and reduces ammoniacal silver nitrate.

Formaldehyde is formed when a mixture of CO and H_2 is treated in an ozoniser (p. 65) and in small quantity when calcium formate is destructively distilled. By cautiously oxidising methyl alcohol with MnO_2 and H_2SO_4 some of the CH_3OH is oxidised to $H{\cdot}CHO$ and combines with more CH_3OH to form *methylal* or *formal* (*methylene dimethyl ether*), $CH_2(OCH_3)_2$, a liquid (b.-p. 42° C.) used as a soporific and as a solvent; when this is distilled with a dilute acid it yields formaldehyde and methyl alcohol.

Paraformaldehyde is a solid polymeride $(CH_2O)_x$ formed when an aqueous solution of formaldehyde is allowed to evaporate; when heated it is converted into another polymeride, *trioxymethylene* or *metaformaldehyde* $(CH_2O)_3$ which melts at 171° C. and then becomes the gas CH_2O. By prolonged contact with lime-water formaldehyde is polymerised to a mixture of sugars (*formose*), a change which may occur, through some agency, in the synthesis of sugar by plants, since formaldehyde has been found in green plants.

Formaldehyde is used in synthetic chemistry for introducing the methylene group (CH_2) into compounds, its oxygen atom readily combining with H_2 and removing them as water, leaving the $:CH_2$ group to take their place, thus: $R{\cdot}NH_2 + O : CH_2 = R{\cdot}N : CH_2 + H_2O$.

Acetic aldehyde, $CH_3{\cdot}CHO$, is obtained by distilling alcohol with potassium bichromate and sulphuric acid. This process requires much care, on account of the violence of the action and the volatility of the aldehyde.

Three parts of potassium bichromate, in crystals free from powder, are placed in a flask or retort surrounded by ice (or by a mixture of sodium sulphate crystals with half their weight of HCl), and a mixture of 2 parts of ordinary alcohol, 4 parts sulphuric acid, and 12 parts of water, also previously cooled in ice, is added. The flask or retort is then connected with a condenser containing iced water, and the refrigerating mixture removed, when the aldehyde will generally be distilled over by the heat attending the reaction. The impure aldehyde thus obtained is re-distilled on the water-bath in the apparatus shown in Fig. 271. The aldehyde,

Fig. 271.—Preparation of aldehyde.

freed from alcohol and aqueous vapour which condense in the inverted condenser, passes over and is dissolved in dry ether contained in the cylinders cooled by ice. The ethereal solution of aldehyde is saturated with dry ammonia, whereupon the

whole of the aldehyde is separated in the form of colourless crystals of *aldehyde-ammonia*, which is sparingly soluble in ether; this is drained upon a filter, and distilled with diluted sulphuric acid in a flask or retort, heated by a water-bath, and connected with a condenser filled with ice water. The aldehyde may be freed from water by standing over fused calcium chloride, and distillation.

The preparation of aldehyde illustrates the use of $K_2Cr_2O_7$ and H_2SO_4 as an oxidising-agent upon organic bodies. Neglecting certain secondary reactions, the production of aldehyde may be represented by the equation—

$$3(CH_3{\cdot}CH_2OH) + K_2O{\cdot}2CrO_3 + 4(H_2O{\cdot}SO_3) = 3(CH_3{\cdot}CHO) + 7H_2O + K_2O{\cdot}SO_3 + Cr_2O_3{\cdot}3SO_3.$$

On a large scale, aldehyde is obtained as a by-product in the manufacture of alcohol, when it comes over with the first portion of the distillate. Commercial alcohol generally contains a little aldehyde.

Aldehyde may also be obtained by distilling a mixture of an acetate and a formate (see above).

Properties of aldehyde.—Sp. gr. 0.80 at 0° C.; boiling-point 20°.8 C. Aldehyde has a peculiar acrid odour, which affects the eyes. It mixes in all proportions with water, alcohol, and ether. It has a great disposition to combine with oxygen to form acetic acid: $CH_3{\cdot}CHO + O = CH_3{\cdot}COOH$. Hence aldehyde acts as a reducing-agent, and one of the tests for it is the reduction of silver from its salts. If a few crystals of aldehyde-ammonia be dissolved in water, a little silver nitrate added, and a gentle heat applied, the silver will be deposited on the sides of the vessel, giving them the reflecting power of a mirror. A *general test for aldehydes* is their power of restoring the red colour to a solution of a salt of rosaniline which has been bleached by sulphurous acid.

Another characteristic property of aldehydes is that of forming crystalline compounds with sodium bisulphite. If aldehyde be mixed with a saturated solution of $NaHSO_3$, it forms a crystalline compound, which is the sodium salt of *ethylidene glycol sulphonic acid*, $CH_3{\cdot}CH(OH)(SO_2ONa)$, combined with H_2O; from this the aldehyde may be obtained by distillation with either acid or alkali.

When mixed with potash, and gradually heated to boiling, most of the paraffin aldehydes yield brown-yellow substances of peculiar odour, known as *aldehyde resins;* their chemical constitution is uncertain.

Nascent hydrogen (water and sodium amalgam) converts aldehyde into alcohol; $CH_3{\cdot}CHO + H_2 = CH_3{\cdot}CH_2{\cdot}OH$ (alcohol).

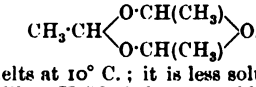
Aldehyde combines with ammonia forming a compound, *aldehyde-ammonia*, which is probably an amine of the hypothetical ethylidene glycol, $CH_3{\cdot}CH(OH)(NH_2)$; with HCN to form *ethylidene cyanohydrin* or *lactonitrile*, $CH_3{\cdot}CH(OH)(CN)$; with alcohol to form *diethyl ethylidene ether* or *acetal*, $CH_3{\cdot}CH(OC_2H_5)_2$, a liquid which boils at 104° C. and is formed in old wine and in the last runnings of spirit stills.

When there is no other compound with which aldehyde can combine, it tends to combine with itself or polymerise.

For example, perfectly pure acetic aldehyde can be kept unchanged, but in the presence of a very little dilute acid or of zinc chloride it is converted into *aldol*, which is a (secondary) alcohol-aldehyde, $CH_3{\cdot}CHOH{\cdot}CH_2{\cdot}CHO$ (*hydroxy-butyric aldehyde*); this resembles aldehyde in appearance and general reactions, but its sp. gr. is 1.120 and it does not distil unchanged; it becomes viscous on standing.

A *condensation* of two or more molecules in this way occurs in many other compounds, and is always termed, by analogy, an *aldol condensation*.

By adding a drop of strong H_2SO_4 to aldehyde, much heat is evolved and the liquid becomes specifically heavier (sp. gr. 0.99 at 20° C.) : this liquid is *paraldehyde*, $C_6H_{12}O_3$, or



It boils at 124° C. and melts at 10° C. ; it is less soluble in hot water than in cold, and when distilled with dilute H_2SO_4 it becomes aldehyde again. *Metaldehyde* is a stereoisomeride of paraldehyde, produced in the same way, but at 0° C. It forms white crystals, insoluble in water, but soluble in ether and in alcohol ; it sublimes when heated to 112° C., without melting, and when heated in a sealed tube at 116° C., it becomes aldehyde again ; the crystals are said to become brittle and opaque after a time, owing to a further polymerisation to $C_8H_{16}O_4$, *tetraldehyde*.

Other characteristic reactions of the aldehydes are the formation of *aldoximes* by reaction with hydroxylamine (p. 103) : $CH_3{\cdot}CHO + H_2{:}N{\cdot}OH = HOH + CH_3{\cdot}CH{:}N{\cdot}OH$ (*acetaldoxime*) ; and the formation of *hydrazones* with phenylhydrazine ; $CH_3{\cdot}CHO + H_2{:}N{\cdot}NHC_6H_5 = HOH + CH_3{\cdot}CH{:}N{\cdot}NHC_6H_5$ (*acetaldehyde hydrazone*.

Aldehyde, in the form of paraldehyde, and some of its derivatives, such as acetal (*v.s.*), are used as soporifics (*cf. chloral*). Aldehyde also finds application in the manufacture of dyes.

352. The chief known homologues of acetic aldehyde are shown in the following table :*

Chemical Name.	Source.	Formula.
Propionic aldehyde	Oxidation of propyl alcohol	$C_2H_5 \cdot CHO$ (49°)
Butyric ,,	,, butyl ,,	$C_3H_7 \cdot CHO$ (74°)
Valeric ,,	,, amyl ,,	$C_4H_9 \cdot CHO$ (102°)
Caproic ,,	Distillation of calcium formate with calcium caproate	$C_5H_{11} \cdot CHO$ (128°)
Œnanthic ,,	Distillation of castor oil	$C_6H_{13} \cdot CHO$ (155°)
Caprylic ,,	,, ,,	$C_7H_{15} \cdot CHO$ (160°)
Rutic ,,	Oil of rue	$C_9H_{19} \cdot CHO$ —
Lauric ,,	,,	$C_{11}H_{23} \cdot CHO$ [44.5°]
Myristic ,,		$C_{13}H_{27} \cdot CHO$ [52.5°]
Palmitic ,,		$C_{15}H_{31} \cdot CHO$ [58.5°]
Stearic ,,		$C_{17}H_{35} \cdot CHO$ [63.5°]

Acetic, propionic, and butyric aldehydes occur among the products of the oxidising action of a mixture of manganese dioxide with sulphuric acid upon albumin, fibrin, and casein.

Thioaldehydes, in which sulphur takes the place of oxygen, are known only in polymeric form, corresponding with the polymerised aldehydes. *Trithioformaldehyde* $(CH_2S)_3$ melts at 216° C., trithioacetadehyde $(CH_3CHS)_3$, occurs in an α and β form melting at 101° and 125° C. respectively. *Mercaptal* is the thio-derivative, corresponding with acetal (p. 582). By oxidation the thio-aldehydes yield trisulphones.

353. **Aldehydes from the Olefine Alcohols.—Acrolein**, or *acrylic aldehyde*, $CH_2{:}CH{\cdot}CHO$, the aldehyde of allyl alcohol, is prepared by distilling glycerine with twice its weight of $KHSO_4$, which abstracts the elements of two molecules of water ; $C_3H_5(OH)_3 = C_2H_3{\cdot}CHO + 2H_2O$. The crude acrolein is shaken with PbO_2 to remove SO_2, and rectified over $CaCl_2$ to remove the water.

Acrolein is a liquid distinguished by a very powerful irritating odour. It has sp. gr. 0·84, and boils at 52° C. It dissolves sparingly in water, but easily in alcohol and ether. Unlike most aldehydes, it does not combine with $NaHSO_3$; but it forms a resinous body with alkali, and reduces ammoniacal $AgNO_3$, which converts it into acrylic acid, $C_2H_3{\cdot}CO_2H$. Sodium amalgam and water (nascent hydrogen) convert it into allyl alcohol, $C_2H_3{\cdot}CH_2OH$. When kept, acrolein becomes a white

* The boiling-points are in round brackets (...), the melting-points in square brackets [...], Centigrade scale. According to the new system the aldehydes are named like the alcohols, the termination *-al* being substituted for *-ol* (see foot-note p. 568).

solid, *disacryl*, probably a polymeride. HCl gas passed into acrolein converts it into a crystalline body, *β-chloropropylaldehyde*, $CH_2Cl{\cdot}CH_2{\cdot}CHO$, which, when distilled with potash, yields *metacrolein*, $C_9H_{12}O_3$ (m.-p. 45° C.), corresponding with paraldehyde.

Crotonic aldehyde, $CH_3{\cdot}CH{:}CH{\cdot}CHO$, is prepared by heating acetic aldehyde to 100° C. for two days in contact with $ZnCl_2$ and a little water. The $ZnCl_2$ acts as a dehydrating agent; $2(CH_3{\cdot}CHO) = H_2O + C_3H_5{\cdot}CHO$ (*aldehyde condensation*). The unchanged aldehyde is distilled off, some water added, and the distillation continued, when water and crotonic aldehyde distil over. It has an irritating odour like acrolein, boils at 104° C., and is sparingly soluble in water. When oxidised by air or silver oxide, it yields crotonic acid, $C_3H_5{\cdot}CO_2H$. It occurs in some kinds of fusel oil.

353*a*. **Aldehydes from Dihydric and Polyhydric Alcohols.**—These may be *di-* or *poly-aldehydes* and *aldehyde-alcohols;* the latter are of much importance, as they include several sugars, like glucose and mannose. These compounds are not considered under this heading, however, for their near relationship to compounds in other classes will be best set forth by treating them in a separate section. The student is therefore referred to the chapter on carbohydrates for a description of the sugars.

Glyoxal, or *oxalic aldehyde*, $CHO{\cdot}CHO$, is prepared by slowly oxidising acetic aldehyde with dilute nitric acid. It occurs among the products of the regulated action of nitric acid on alcohol and glycol. (See p. 575.)

It is a deliquescent solid, soluble, in water, alcohol, and ether, forming a crystalline compound with two mols. $NaHSO_3$, and reducing silver nitrate, becoming oxidised to oxalic acid, $CO_2H{\cdot}CO_2H$, and glyoxylic acid, $CHO{\cdot}CO_2H$. Alkalies oxidise one CHO group and reduce the other, forming glycollic acid, $CH_2OH{\cdot}COOH$. With ammonia, it yields *glycosine:* $3C_2H_2O_2 + 4NH_3 = 6H_2O + N_4(C_2H_2)_3$. Glyoxal combines with 2HCN to form the nitrile of tartaric acid, $CH(OH)(CN){\cdot}CH(OH)(CN)$.

Glyceric aldehyde or *glycerose*, $CH_2OH{\cdot}CHOH{\cdot}CHO$, is an aldehyde-alcohol obtained by the careful oxidation of glycerol (p. 577). By condensation it is converted into *acrose*, one of the sugars.

354. **Aldehydes from the Aromatic Alcohols.—Benzaldehyde**, *benzoic aldehyde*, or *bitter-almond oil*, $C_6H_5{\cdot}CHO$, was originally made by distilling the moistened bitter-almond cake from which the *fixed* oil had been extracted by pressure. The cake was placed in a perforated vessel and subjected to the action of steam, which carried over the oil and deposited it as a heavy layer on standing.

The bitter-almond oil does not exist ready formed in the almond, but is a product of the decomposition of the bitter substance, *amygdalin*, $C_{20}H_{27}NO_{11}$, of which the bitter almond contains about 5 per cent. This substance is a glucoside, and is decomposed, in the presence of water and of a peculiar albuminoid ferment present in the almond and known as *emulsin*,* into glucose, bitter almond-oil, and hydrocyanic acid, $C_{20}H_{27}NO_{11} + 2H_2O = 2C_6H_{12}O_6 + C_7H_6O + HCN$. The presence of hydrocyanic acid renders the crude oil of bitter almonds poisonous. It may be purified either by re-distilling with lime and ferrous chloride, when the HCN is converted into a ferrocyanide; or by shaking it with an equal volume of a strong solution of $NaHSO_3$, which combines with the benzoic aldehyde to form a crystalline compound, from which the pure oil may be obtained by distillation with sodium carbonate.

Benzaldehyde is now made artifically from toluene. When chlorine is passed into boiling toluene, preferably in sunlight, *benzal chloride*,

* The terms *zymase*, *enzyme*, and *hydrolyst* have been applied to such *unorganised ferments*.

$C_6H_5{\cdot}CHCl_2$, is produced. By heating this with lime under pressure, it is converted into bitter-almond oil—

$$C_6H_5{\cdot}CHCl_2 + Ca(OH)_2 = CaCl_2 + H_2O + C_6H_5{\cdot}CHO.$$

Or the chlorination of the toluene is stopped when benzyl chloride, $C_6H_5{\cdot}CH_2Cl$, has been formed, and this is then heated with lead nitrate—

$$2C_6H_5{\cdot}CH_2Cl + Pb(NO_3)_2 = 2C_6H_5{\cdot}CHO + PbCl_2 + 2HNO_2.$$

Benzoic aldehyde is a colourless or pale yellow liquid, of characteristic odour, boiling at 179° C., and of sp. gr. 1.05. It is very sparingly soluble in water, but dissolves in alcohol, and is precipitated on addition of water. It is often sold in alcoholic solution. The oxidising action of air gradually converts benzoic aldehyde into crystals of benzoic acid; $C_6H_5{\cdot}CHO + O = C_6H_5{\cdot}CO_2H$. The presence of hydrocyanic acid retards this conversion.

The aromatic aldehydes show reactions very similar to those of the fatty aldehydes. They are, however, less powerful reducing-agents, and instead of resinifying with alkalies, they are converted into the corresponding alcohol and acid, one part being reduced and the other oxidised: $2C_6H_5{\cdot}CHO + KOH = C_6H_5{\cdot}CH_2OH + C_6H_5{\cdot}COOK$.

Moreover, with NH_3 they do not combine directly, but are converted into compounds like *hydrobenzamide*, a crystalline substance, m.-p. 110° C.; $3(C_6H_5{\cdot}CHO) + 2NH_3 = (C_6H_5{\cdot}CH)_3{\cdot}N_2 + 3H_2O$.

They show a remarkable tendency to condense with other compounds under influence of dehydrating agents, the aldehydic oxygen combining with two H atoms from the other compound. Thus by action of HCl gas on a mixture of benzaldehyde and acetic aldehyde, cinnamic aldehyde is formed; $C_6H_5CHO + CH_3{\cdot}CHO = C_6H_5{\cdot}CH : CH{\cdot}CHO + H_2O$.

Benzaldehyde dissolves in a strong solution of Na_2SO_3, and if dilute H_2SO_4 be added, drop by drop, to the solution, voluminous crystals of $C_6H_5{\cdot}CHO{\cdot}NaHSO_3$ are deposited; these dissolve on heating but are deposited again on cooling. By reduction with Na-amalgam, benzaldehyde yields benzyl alcohol and hydrobenzoin (p. 575).

Benzaldoxime, $C_6H_5{\cdot}CH : N{\cdot}OH$ exists in an α-form (m.-p. 35° C.), and a β-form (m.-p. 125° C.), which passes into the α-form when heated. These are stereoisomerides (*see acetoximes*).

Cuminic, or *cumic aldehyde*, or *cuminol*, is 1 : 4-*isopropylbenzaldehyde*, $C_6H_4{\cdot}C_3H_7{\cdot}CHO$, and occurs in the aromatic oils of cummin, caraway, and water-hemlock, all umbelliferous plants; it is extracted from the oil by shaking with solution of $NaHSO_3$, which forms a crystalline compound with it. It is liquid, fragrant, and boils at 235° C.

Cinnamic aldehyde, $C_6H_5{\cdot}CH : CH{\cdot}CHO$, occurs in the essential oils of cinnamon and cassia, and is very similar in its chemical properties to benzaldehyde. When oxidised, it yields *cinnamic acid*, $C_8H_7{\cdot}CO_2H$. It may be obtained from benzoic and acetic aldehydes, as above mentioned.

355. The **hydroxy-aromatic aldehydes, like salicylic aldehyde**, $C_6H_4(OH){\cdot}CHO$ (*hydroxybenzaldehyde*), have an OH attached directly to the benzene ring, and are therefore phenol aldehydes, corresponding with the phenol alcohols (p. 571). Besides their formation by oxidation of these alcohols, the hydroxy-aromatic aldehydes are produced by a nucleal condensation between the phenols and chloroform, produced by heating the mixture with aqueous alkali (Reimer's reaction).

$$C_6H_5{\cdot}OH + CHCl_3 + 4KOH = C_6H_4(OK){\cdot}CHO + 3KCl + 3HOH.$$

Phenol. Chloroform. Potassium salicylaldehyde.

The potassium compound is distilled with dilute acid to obtain the aldehyde.

In this reaction the alkali is required to absorb the HCl which is formed when water alone is used, and which must be removed to prevent back action. the change being reversible.

Salicyl aldehyde is *ortho*-hydroxybenzaldehyde, there being, of course, three isomerides of this disubstitution product. It exists in *oil of spiræa* (meadow-sweet), and is made by oxidising saligenin (p. 572), or from phenol as described above. Its sp. gr. is 1.17, and it boils at 196° C. It dissolves in alcohol, but sparingly in water. It resembles benzaldehyde in most reactions but exhibits some characteristic of its phenol character, such as the ferric chloride coloration and the exchange of H for K by treatment with KOH forming $C_6H_4(OK)\cdot CHO$. Like other orthohydroxyaldehydes it stains the skin yellow.

Anisic aldehyde, $C_6H_4(OCH_3)\cdot CHO$. is *paramethoxybenzaldehyde*, the methyl derivative of parasalicylic aldehyde; it is prepared by heating the essential oils of anise and fennel (both umbelliferous plants) with dilute HNO_3, being formed by the oxidation of anethol (*q.v.*) which these oils contain. It is a fragrant liquid, boiling at 248° C.

Dihydroxybenzaldehydes are also known. The 1 : 3 : 4-derivative, *protocatechuic aldehyde*, $C_6H_3(OH)_2\cdot CHO[CHO : (OH)_2 = 1 : 3 : 4]$ is obtained from pyrocatechol, $C_6H_4(OH)_2$, and chloroform by Reimer's reaction (*r.s.*); it melts at 153° C. When *methylpyrocatechol*, $C_6H_4(OH)(OCH_3)$, is similarly treated it yields the methyl derivative of protocatechuic aldehyde, $C_6H_3(OH)(OCH_3)\cdot CHO$; this is *vanillin*, an aromatic substance, much used for flavouring, extracted from the pods of *Vanilla planifolia*, a Mexican orchidaceous plant, by boiling them with alcohol. It forms needles, melts at 80° C., and sublimes. It is sparingly soluble in water. Vanillin is now made artificially by oxidising *coniferine*, $C_{16}H_{22}O_8$, by chromic acid. Coniferine is a crystalline glucoside, extracted from pinewood; when oxidised it yields *glycovanillin*, the glucoside of vanillin, $C_6H_3(OCH_3)(O\cdot C_6H_{11}O_5)\cdot CHO$, which yields glucose and vanillin on hydrolysis.

Piperonal or *heliotropine* is *methyleneprotocatechuic aldehyde* $C_6H_3(O_2CH_2)\cdot CHO$, made by oxidising piperic acid (*q.v.*) It melts at 263° C. and is valued for its odour of heliotrope.

356. **Pyromucic aldehyde, furfural**, or *furfurol*, $C_4H_3O\cdot CHO$, is the aldehyde of furfurane (*q.v.*), $O\begin{matrix}C(CHO) : CH\\ CH = = = CH\end{matrix}$. It is prepared by distilling the bran of wheat, freed from starch and gluten by steeping in a cold weak solution of potash, with half its weight of sulphuric acid, previously diluted with an equal bulk of water, a current of steam being forced through the mixture; the furfural distils over with the water, from which it may be separated by adding common salt. A hundred parts of bran yield about three of furfural. It is a product of the hydrolysis of certain carbohydrates, particularly such as are *pentoses*. It is also present in fusel oil from crude spirits. Furfural is a colourless liquid smelling of bitter almonds, of sp. gr. 1.17 and boiling-point 162° C. It dissolves in twelve times its weight of water, and is freely soluble in alcohol. Strong sulphuric acid dissolves it to a purple liquid, from which water precipitates it unchanged. It becomes brown when exposed to the air. Furfural combines with $NaHSO_3$, reduces silver, and yields an intense red colour with aniline acetate. With ammonia it behaves as an aromatic aldehyde, forming *furfuramide* $(C_4H_3O\cdot CH)_3N_2$, in which three molecules of furfural have exchanged O''_3 for N'''_2.

By oxidation, furfural is converted into *pyromucic acid*, $C_4H_3O\cdot CO_2H$. Alcoholic solution of potash converts it into potassium pyromucate and *furfuryl alcohol*, $C_4H_3O\cdot CH_2OH$.

Fucusol is isomeric with furfural, and is prepared, in a similar way, from certain varieties of *fucus* (seaweed).

III. ACIDS.

357. **The acids are the second oxidation-products of the primary alcohols. The group $\cdot C\begin{matrix}H_2\\ OH\end{matrix}$ in the alcohol is converted into $\cdot C\begin{matrix}O\\ OH\end{matrix}$, *carboxyl*, in the acid, so that a general formula for an acid is R·COOH, where R is a**

hydrocarbon residue or radicle. This view of the constitution of acids is supported mainly by the three following facts: (1) Two acids can be synthetised from sodium-substituted hydrocarbons and CO_2, showing that the acid produced (or its sodium salt) probably contains the hydrocarbon radicle and both the oxygen atoms attached to the same carbon atom; *e.g.*, $CH_3Na + CO_2 = CH_3{\cdot}COONa$. (2) The monochlorohydrocarbons, *e.g.*, $CH_3{\cdot}CH_2Cl$, can be converted by double decomposition with KCN into cyanides, *e.g.*, $CH_3{\cdot}CH_2{\cdot}C \vdots N$, and when these are boiled with water the N is removed as NH_3, and an acid remains; $CH_3{\cdot}CH_2{\cdot}C \vdots N + 2HOH = CH_3{\cdot}CH_2{\cdot}COOH + NH_3$. (3) The acids contain a hydroxyl group, for, by interaction with PCl_5, they exchange O and H for Cl, hydrogen chloride being evolved (p. 579):

$$CH_3{\cdot}COOH + PCl_5 = CH_3{\cdot}COCl + POCl_3 + HCl.$$

It will be found that the formula H·COOH is the only formula which can be written for formic acid, which resembles all the other acids in its behaviour.

Two methods generally applicable for producing the acids are—(1) oxidation of the corresponding alcohol, $R{\cdot}CH_2OH + O_2 = R{\cdot}COOH + HOH$, and (2) hydrolysis (p. 265) of the cyanogen derivatives of the corresponding hydrocarbons, $R{\cdot}CN + 2HOH = R{\cdot}COOH + NH_3$.

Isomerism among the acids is confined to the hydrocarbon radicles in them; thus there will be two acids of the formula $C_3H_7{\cdot}COOH$, since there are two propyl radicles.

The basicity of an acid (p. 104) is found to be limited by the number of COOH groups which it contains, thus showing that it is the H in this group which is exchanged for metals to form salts. When an acid contains two CO_2H groups, it is a *dibasic* acid, or if there are three CO_2H groups, it is a *tribasic* acid, and so on.

358. **Acids from Monohydric Paraffin Alcohols (Acetic or Fatty Series).**—The acids originally obtained by decomposing soap with a mineral acid were termed fatty acids because the soap had been made by saponifying fat. Later, the more important of them were shown to belong to the same series of acids as acetic acid, hence the term fatty acids was applied to the series.

The fatty acids correspond with the general formula $C_nH_{2n+1}{\cdot}COOH$ and are produced, by two general methods given above, from the alcohols and cyanides of the paraffin series.

An important method of obtaining fatty acids consists in treating alkyl derivatives of ethyl acetoacetate (*q.v.*) with an alkali. This compound, $CH_3CO{\cdot}CH_2{\cdot}COOC_2H_5$, contains a CH_2 group, attached to two CO groups; where this is the case Na can substituted for the H in the CH_2 and by treating the sodium derivative with an alkyl iodide, compounds of the type $CH_3CO{\cdot}CHR{\cdot}COOC_2H_5$ and $CH_3CO{\cdot}CR_2{\cdot}COOC_2H_5$ are obtained. By treatment with potash these yield potassium acetate, the potassium salt of a new fatty acid and ethyl alcohol:

$$CH_3CO{\cdot}CHR{\cdot}COOC_2H_5 + 2KOH = CH_3COOK + CH_2RCOOK + C_2H_5OH$$
$$CH_3CO{\cdot}CR_2{\cdot}COOC_2H_5 + 2KOH = CH_3COOK + CHR_2COOK + C_2H_5OH$$

In the latter case the acid contains a secondary radicle. The reaction is sometimes complicated by the formation of a ketone.

The ethyl salt of the dibasic acid malonic acid, $CH_2(COOH)_2$, also contains a CH_2 group attached to two CO groups, so that when it is appropriately treated, first Na or Na_2 and then one or two alkyl groups may be substituted for the H in the CH_2 group. In this way compounds of the type $CHR(COOC_2H_5)_2$ and $CR_2(COOC_2H_5)_2$ and from these the corresponding acids $CHR(COOH)_2$ and $CR_2(COOH)_2$ are obtained. When heated, these acids lose CO_2, yielding acids of

the acetic series. The preparation of ethyl malonate, $CH_2(COOC_2H_5)_2$, is described later; the reactions by which it may be converted into butyric acid, for example, are as follows:

$$CH_2(COOC_2H_5)_2 + C_2H_5ONa = CHNa(COOC_2H_5)_2 + C_2H_5OH$$
$$CHNa(COOC_2H_5)_2 + C_2H_5I = CHC_2H_5(COOC_2H_5)_2 + NaI$$
$$CHC_2H_5(COOC_2H_5)_2 + 2KOH = CHC_2H_5(COOK)_2 + 2C_2H_5OH$$
$$CHC_2H_5(COOK)_2 + 2HCl = CHC_2H_5(COOH_2) + 2KCl$$
$$CHC_2H_5(COOH)_2 \text{ (heated)} = CH_2C_2H_5(COOH) + CO_2$$

As malonic acid can be made from acetic acid (p. 614) this series of reactions serves for the preparation of the homologues of acetic acid from the acid itself.

The principal members of the series are :—

Monobasic acids of the acetic series, $C_nH_{2n+1}CO_2H$.

Acid.	Source.	Formula.	M.-P.	B.-P.
Formic	Red ants, nettles	$H \cdot CO_2H$	9° C.	100.6° C.
Acetic	Vinegar	$CH_3 \cdot CO_2H$	17° C.	118° C.
Propionic	Oxidation of oils	$C_2H_5 \cdot CO_2H$	−22° C.	140° C.
Butyric	Rancid butter	$C_3H_7 \cdot CO_2H$	− 8° C.	163° C.
Valeric	Valerian root	$C_4H_9 \cdot CO_2H$	−59° C.	186° C.
Caproic	Rancid butter	$C_5H_{11} \cdot CO_2H$	8° C.	205° C.
Œnanthic	Oxidation of castor oil	$C_6H_{13} \cdot CO_2H$	−11° C.	223° C.
Caprylic	Rancid butter	$C_7H_{15} \cdot CO_2H$	7° C.	237° C.
Pelargonic	Geranium leaves	$C_8H_{17} \cdot CO_2H$	13° C.	254° C.
Rutic or Capric	Rancid butter	$C_9H_{19} \cdot CO_2H$	31° C.	268° C.
Undecylic	Oil of rue	$C_{10}H_{21} \cdot CO_2H$	29° C.	—
Lauric	Bay berries	$C_{11}H_{23} \cdot CO_2H$	44° C.	—
Tridecylic	Cocoa-nut oil	$C_{12}H_{25} \cdot CO_2H$	41° C.	—
Myristic	Nutmeg-butter	$C_{13}H_{27} \cdot CO_2H$	54° C.	—
Pentadecylic	*Agaricus integer* (a fungus)	$C_{14}H_{29} \cdot CO_2H$	51° C.	—
Palmitic	Palm oil	$C_{15}H_{31} \cdot CO_2H$	62° C.	—
Margaric		$C_{16}H_{33} \cdot CO_2H$	60° C.	—
Stearic	Tallow	$C_{17}H_{35} \cdot CO_2H$	69° C.	—
Arachidic or Butic	Butter: earth-nut	$C_{19}H_{39} \cdot CO_2H$	77° C.	—
Behenic	Oil of ben	$C_{21}H_{43} \cdot CO_2H$	84° C.	—
Cerotic	Bees'-wax	$C_{25}H_{51} \cdot CO_2H$	78° C.	—
Melissic	„	$C_{29}H_{59} \cdot CO_2H$	91° C.	—

As in other homologous series, the volatility of the acids decreases as the number of carbon atoms increases, so that palmitic acid and those richer in carbon can be distilled only under diminished pressure or in a current of superheated steam. The solubility in water diminishes in the same order; acetic acid mixes with water in all proportions while palmitic acid is quite insoluble. With the exception of formic and acetic acids they are decidedly oily in character.

The acid strength also diminishes with the increase in the carbon atoms, and this is turned to account in separating the volatile fatty acids from each other by the *method of partial saturation*. Suppose it to be required to separate butyric and valeric acids. The mixture is divided into equal parts, one of which is exactly neutralised by soda, yielding butyrate and valerate of sodium. The other half of the acid mixture is then added, and the whole distilled. Since butyric acid is the stronger acid, it will expel the valeric acid from the sodium valerate. If the mixture contained equal molecules of the two acids, the distillate would contain valeric acid only, and the residue would contain the sodium butyrate. If the valeric acid preponderated, the residue would contain both valerate and butyrate, and, when distilled with sulphuric acid, would yield a fresh mixture of the acids, which could be again treated in the same way. But if butyric acid preponderated, the residue would be only sodium butyrate, while the distillate would contain both butyric and valeric acids, to be again treated by partial saturation.

The non-volatile fatty acids may be separated from each other by *fractional precipitation*, which depends on the principle that the insolubility of their barium,

magnesium, and lead salts increases with the number of carbon atoms. The mixture of fatty acids is dissolved in alcohol, and is *partially* precipitated by an alcoholic solution of the acetate of Ba, Mg, or Pb. This precipitate will contain the acid or acids richest in carbon. It is filtered off, and another precipitate is obtained from the solution in the same way. This will contain acids poorer in carbon, and so on. Each precipitate is decomposed by HCl, and the new mixture of acids so obtained is subjected to the same treatment, until the separated acid is found to have a constant melting-point.

The constitution of the fatty acids is disclosed when they are subjected to electrolysis, for they then evolve one atom of carbon as CO_2; thus, acetic acid yields dimethyl (ethane), CO_2 and H—

$$2(CH_3{\cdot}CO_2H) = (CH_3)_2 + 2CO_2 + H_2.$$

Again, valeric acid yields dibutyl, CO_2 and H—

$$2(C_4H_9{\cdot}CO_2H) = (C_4H_9)_2 + 2CO_2 + H_2.$$

To prepare an acid higher in the series from one lower in the series, advantage may be taken of such reactions as the following:

(1) $CH_3{\cdot}CH_2{\cdot}COOH + H_4 = CH_3{\cdot}CH_2{\cdot}CH_2OH.$
(2) $3CH_3{\cdot}CH_2{\cdot}CH_2OH + PI_3 = 3CH_3{\cdot}CH_2{\cdot}CH_2I + P(OH)_3.$
(3) $CH_3{\cdot}CH_2{\cdot}CH_2I + KCN = CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CN + KI.$
(4) $CH_3{\cdot}CH_2{\cdot}CH_2CN + 2HOH = CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}COOH + NH_3.$

359. **Formic acid, $H{\cdot}CO_2H$,** was originally obtained from ants. It occurs in nettles and other plants, in some animal fluids, and occasionally in mineral waters. It is prepared by distilling oxalic acid with glycerine. 30 grams of crystallised oxalic acid and 200 c.c. of glycerine are heated, in a half-litre flask provided with a thermometer and condenser, to about 80° C., when formic acid distils over together with the water of crystallisation of the oxalic acid, and carbonic acid gas is evolved; $CO_2H{\cdot}CO_2H = H{\cdot}CO_2H + CO_2$. When the evolution of CO_2 ceases, a fresh quantity of oxalic acid may be introduced and the operation continued, the same glycerine serving for the conversion of a large quantity of oxalic acid. The formic acid first produced converts the glycerine into *monoformin*—

$$C_3H_5(OH)_3 + H{\cdot}CO_2H = C_3H_5(OH)_2(O.CHO) + HOH.$$

The monoformin is then decomposed by the water of crystallisation of the oxalic acid, the equation being reversed, and glycerine being reproduced. By continuing the process, formic acid of 56 per cent. may be obtained. To prepare the pure acid, this is neutralised with lead oxide, the lead formate crystallised, dried, and heated to 100° C. in a current of dry H_2S; $(H{\cdot}CO_2)_2Pb + H_2S = 2H{\cdot}CO_2H + PbS$. The formic acid is carefully condensed and redistilled with a little lead formate to remove H_2S.

Formic acid is obtained synthetically by heating caustic alkalies to 100° C. in carbonic oxide; $CO + KOH = H{\cdot}CO_2K$ (potassium formate); again, potassium, acting on carbon dioxide in presence of water, yields acid potassium carbonate and potassium formate—

$$2CO_2 + H_2O + K_2 = KHCO_3 + H{\cdot}CO_2K.$$

It is also produced in other reactions in which carbonic acid is acted on by reducing-agents. Carbonic acid may be regarded as *hydroxyformic acid*, $HO{\cdot}CO_2H$, that is, formic acid, $H{\cdot}CO_2H$, in which OH is substituted for H. When starch and other organic bodies are violently oxidised, they yield carbonic acid, but if they are gradually and quietly

oxidised, they yield formic acid. The quiet oxidation of organic bodies is often effected by heating them with MnO_2 and dilute H_2SO_4.

Formic acid is also formed by oxidising methyl alcohol, and when hydrocyanic acid is hydrolysed by boiling it with dilute acids, $H{\cdot}CN + 2HOH = H{\cdot}CO_2H + NH_3$.

Properties of formic acid.—Colourless liquid, fuming slightly in air and of pungent smell; it blisters the skin. Formic acid boils at 100°.6 C. and melts at 9°. Its sp. gr. is 1.22 at 20°. The diluted acid boils at a higher temperature; an acid of 77 per cent. boils at 107°.

The *formates* are all soluble in water; their solutions yield a red colour with ferric chloride, and reduce silver from the nitrate, when boiled with it, on account of the tendency of formic acid to become carbonic (hydroxyformic) acid. Solid formates evolve carbonic oxide (burning with a blue flame) when heated with strong H_2SO_4, which removes the elements of water; $H{\cdot}CO_2H = HOH + CO$. A formate heated with excess of baryta yields the oxalate; $(HCO_2)_2Ba = (CO_2)_2Ba + H_2$.

Formic acid is used in making some of the coal-tar dyes.

Formic acid differs in some respects from the other members of the series. Thus its powerful reducing action relates it to the aldehyde acids (p. 607); indeed, if its formula be written $HO{\cdot}CHO$ it might be regarded as *hydroxyformaldehyde*. No acid chloride or anhydride, such as are characteristic derivatives of the higher acids of the series, can be obtained from formic acid. By loss of water it yields CO not $(H{\cdot}CO)_2O$, which would be the true anhydride. When heated at 160° C. it breaks up into H & CO_2, the same change occurring at the ordinary temperature in contact with platinum black.

360. **Acetic acid,** or *methyl-formic acid,* $CH_3{\cdot}CO_2H$, is found either free or combined in many plants and in some animal fluids. It is obtained by the destructive distillation of wood or of sawdust, or spent dye-woods. The aqueous layer in the condenser (p. 566) is neutralised by sodium carbonate, and the methyl alcohol and acetone are distilled off. The evaporated liquor deposits impure crystals of sodium acetate which are heated to expel some tarry matters, and distilled with H_2SO_4, when acetic acid passes over; $CH_3{\cdot}CO_2Na + H_2SO_4 = CH_3{\cdot}CO_2H + NaHSO_4$. The crude acid from wood is termed *pyroligneous acid.*

Acetic acid is also made by the oxidation of alcohol for the production of vinegar; $CH_3{\cdot}CH_2{\cdot}OH$ (ethyl alcohol) $+ O_2 = CH_3{\cdot}CO_2H + H_2O$. But this equation cannot be realised unless some third substance be present. It was seen at p. 564 that platinum black would answer the purpose, and in some chemical works this process has been employed for making acetic acid. Weak fermented liquors, such as beer and the lighter wines, are very liable to become sour, which is never the case with distilled spirits, however much diluted. This is due to the presence in the fermented liquid of albuminous (nitrogenised) matters and salts, which afford nourishment to a microscopic organism, termed *Mycoderma aceti,* which appears to convey the oxygen of the air to the alcohol.

Quick vinegar process.—A weak spirit mixed with a little yeast or beet-root juice, heated to about 27° C., is caused to trickle slowly from pieces of cord fixed in a perforated shelf over a quantity of wood shavings previously soaked in vinegar to impregnate them with the acetic ferment or *mother of vinegar.* The shavings are packed in a tall cask (Fig. 272) in which holes have been drilled in order to allow the passage of air. The oxidation of the alcohol soon raises the temperature to about 38° C., which occasions a free circulation of air among the

shavings. The mixture is passed three or four times through the cask, and in about thirty-six hours the conversion into vinegar is completed. If the supply of air be insufficient, alcohol is lost in the form of aldehyde vapour, the irritating odour of which pervades the air of the factory.

White-wine vinegar is prepared from light wines by a similar process. Malt vinegar is made from infusion of malt fermented by yeast with free contact of air. Vinegar contains, on an average, about 5 per cent. of acetic acid. Its aroma is due to the presence of a little acetic ether. The vinegar of commerce is allowed to be mixed with $\frac{1}{150}$ of its weight of sulphuric acid in order to prevent it from becoming mouldy. By distilling vinegar a weak acetic acid is obtained, which may be concentrated by redistilling and receiving separately the portion distilling between 110° and 120° C.

Fig. 272.

Pure acetic acid is prepared by distilling 5 parts by weight of fused sodium acetate with 6 parts of concentrated sulphuric acid (see above). The distillate may be redistilled with a little MnO_2 to remove SO_2.

The acid is also produced when CH_3Na is treated with CO_2 (p. 587), and when methyl cyanide is hydrolysed by boiling dilute acids; $CH_3{\cdot}CN + 2HOH = CH_3{\cdot}COOH + NH_3$.

Properties of acetic acid.—Colourless, pleasant smell, blistering the skin, boiling at 118° C., and giving a vapour which burns with a flame like that of alcohol. Its true melting-point is 17° C., but it may be cooled far below this without solidifying, unless a crystal of the acid be introduced, when the whole crystallises in beautiful plates; hence the term *glacial acetic acid.* The sp. gr. of the pure acid is 1.063 at 18°, but the strength of the acid cannot, as in other cases, be inferred from the sp. gr., because the latter is increased by addition of water, till it reaches 1.079 (70 per cent. of acid), when it is diminished by more water, so that a 43 per cent. acid has the same sp. gr. as the pure acid.

Acetic acid is one of the most stable of the organic acids. It is unattacked by most oxidising-agents. When its vapour is passed through a red-hot tube it yields several products, among which marsh gas and acetone are conspicuous. Most of its salts are soluble in water, so that it is not easily precipitated; but if it be exactly neutralised by ammonia, and stirred with silver nitrate, a crystalline precipitate of *silver acetate*, $CH_3{\cdot}CO_2Ag$, is obtained; *mercurous acetate*, $CH_3{\cdot}CO_2Hg$, may be obtained in a similar way. Ferric chloride added to the neutral solution gives a fine red colour.

361. Many of the acetates are employed in the arts. Those formed by the weaker bases, such as Fe_2O_3 and Al_2O_3, are easily decomposed by boiling with water, basic acetates being precipitated; hence the *aluminium acetate* and *ferric acetate* (*red liquor*) are much used by dyers and calico-printers as *mordants*, the basic acetates being deposited in the fabric, and forming insoluble compounds with colouring-matters.

Lead acetate, or *sugar of lead*, $(CH_3CO_2)_2Pb.3Aq$, is the commonest commercial acetate, and is prepared by dissolving litharge (PbO) in an excess of acetic acid, when the solution deposits prismatic crystals of the salt. On the large scale, acetic acid vapour is passed through copper vessels with perforated shelves on which litharge is placed. Lead acetate is intensely sweet and very soluble in

water (1½ part). Commonly, the solution is turbid from the precipitation of lead carbonate by the carbonic acid in the water; a drop of acetic acid clears it. The acetate is soluble in alcohol. When heated, it fuses at 75° C. and becomes anhydrous at 100°. The anhydrous salt melts when further heated, evolves the pleasant smell of acetone, and becomes again solid as a basic lead acetate, which is decomposed at a higher temperature, evolving CO_2 and acetone, and leaving a yellow residue of PbO mixed with globules of lead.

There are several basic lead acetates, but the only one of practical importance is the *tribasic lead acetate, Goulard's extract* $(CH_3{\cdot}CO_2)_2Pb.2PbO.H_2O$, which is prepared by boiling lead acetate with litharge. It forms needle-like crystals, which are very soluble in water, but insoluble in alcohol. A strong solution of the salt is not affected by the air, but a weak solution is rendered turbid by the smallest quantity of CO_2 in air or water. Tribasic lead acetate is very useful in the laboratory for precipitating tannin, gum, &c., from vegetable infusions in order to extract the alkaloids.

Verdigris is a mixture of several basic cupric acetates prepared by acting on sheet copper with the refuse grapes of the wine-press, which yield acetic acid by oxidation of the alcohol: the acid combines with the cupric oxide formed by the action of air upon the copper. Commercial verdigris consists chiefly of the compound $(CH_3{\cdot}CO_2)_2Cu.CuO.6H_2O$. When this is treated with water it is only partly dissolved, the residue having the composition $(CH_3{\cdot}CO_2)_2Cu.2CuO.2H_2O$. By dissolving verdigris in acetic acid, the normal cupric acetate may be obtained in crystals of the formula $(CH_3{\cdot}CO_2)_2Cu.H_2O$. It forms blue prisms soluble in water. Verdigris is used in the manufacture of colours, and in dyeing and calico-printing.

Emerald-green or *cupric aceto-arsenite*, $(CH_3{\cdot}CO_2)_2Cu.Cu_3(AsO_3)_2.As_4O_6$, is made by boiling verdigris with white arsenic and water. It is used for colouring wall-paper and other fabrics, and is dangerous to the makers and purchasers.

Sodium acetate, $CH_3.CO_2Na.3Aq$, prepared by neutralising acetic acid with sodium carbonate, crystallises in prisms which are very soluble in water, and yields one of the best examples of a supersaturated solution (see p. 51), which is used in foot-warmers for railway carriages, on account of the continuous evolution of heat during its crystallisation. It is four times as effective as an equal volume of water.

The acetates of sodium and potassium are remarkable for their fusibility and their stability at high temperatures; they do not carbonise so readily as do most salts of organic acids. Potassium, sodium, and ammonium acetates combine with one and with two molecules of acetic acid to form crystalline compounds.

Calcium acetate, when dissolved in water together with $CaCl_2$, yields the compound $(CH_3{\cdot}COO)_2Ca.CaCl_2.10Aq$, which crystallises easily, and is sometimes produced for effecting the purification of crude acetic acid (Condy's patent).

Zinc acetate, $(CH_3{\cdot}CO_2)_2Zn.3Aq$, is remarkable for being capable of sublimation at a moderate heat, when dried.

Acetic acid is very useful in organic chemistry as a simple solvent, especially for resins and hydrocarbons, such as naphthalene and anthracene.

362. Acetic acid may be produced by the reaction of zinc methyl, $Zn(CH_3)_2$, with $COCl_2$ (p. 190) which yields acetyl chloride (*q.v.*), a compound which furnishes acetic acid when decomposed by water—

$$Zn(CH_3)_2 + 2COCl_2 = 2CH_3{\cdot}COCl + ZnCl_2. \quad CH_3{\cdot}COCl + HOH = CH_3{\cdot}COOH + HCl.$$

The group $CH_3{\cdot}CO$, which remains unchanged during the latter reaction is termed *acetyl*, C_2H_3O, and may be regarded as ethyl, $CH_3{\cdot}CH_2$, in which O″ has been substituted for H_2.

There is a similar *acid radicle* corresponding with each *alcohol radicle*: a few examples are here given—

Alcohol radicles.		*Acid radicles.**	
Methyl	CH_3	Formyl	CHO
Ethyl	$CH_3{\cdot}CH_2$	Acetyl	$CH_3{\cdot}CO$
Propyl	$C_2H_5{\cdot}CH_2$	Propionyl	$C_2H_5{\cdot}CO$
Butyl	$C_3H_7{\cdot}CH_2$	Butyryl	$C_3H_7{\cdot}CO$
Amyl	$C_4H_9{\cdot}CH_2$	Valeryl	$C_4H_9{\cdot}CO$

* Termed *acidyl* or *acyl* radicles.

It will be seen later that the alcohol radicles combine in pairs with oxygen to produce *ethers* of the type $\begin{matrix}R\\R\end{matrix}\!\!>\!O$, the two radicles being the same or different. The acid radicles combine with oxygen in a similar manner to produce *acid anhydrides*, such as $\begin{matrix}CH_3CO\\CH_3CO\end{matrix}\!\!>\!O$, *acetic anhydride*, $\begin{matrix}CH_3CO\\C_2H_5CO\end{matrix}\!\!>\!O$, *aceto-propionic anhydride.*

Acetic anhydride, or *di-acetyl oxide*, or *anhydrous acetic acid* $(CH_3{\cdot}CO)_2O$, is prepared by distilling acetyl chloride with an equal weight of perfectly anhydrous sodium acetate; $CH_3COCl + CH_3{\cdot}COONa = (CH_3{\cdot}CO)_2O + NaCl$. It distils over as a colourless liquid, smelling of acetic acid, but irritating the eyes; its sp. gr. is 1.073, and boiling-point, 137° C. It dissolves slowly in water, with evolution of heat and formation of acetic acid $(CH_3{\cdot}CO)_2O + H_2O = 2(CH_3{\cdot}COOH)$.

Acetic anhydride may also be formed by heating lead acetate with carbon disulphide; $2Pb(CH_3{\cdot}CO_2)_2 + CS_2 = 2(CH_3{\cdot}CO)_2O + 2PbS + CO_2$. Also by heating acetyl chloride with anhydrous oxalic acid; $C_2H_3OCl + (COOH)_2 = (C_2H_3O)_2O + HCl + CO + CO_2$.

By carefully acting on acetic anhydride with sodium-amalgam and water (or snow), it has been converted into aldehyde and alcohol—

$(CH_3{\cdot}CO)_2O + 2H_2 = 2(CH_3{\cdot}CHO) + H_2O$, and $CH_3{\cdot}CHO + H_2 = CH_3{\cdot}CH_2{\cdot}OH$. With HCl it yields acetyl chloride and acetic acid, $(CH_3CO)_2O + HCl = CH_3COCl + CH_3COOH$.

Acetyl dioxide, or *acetic peroxide*, $(CH_3{\cdot}CO)_2O_2$, is obtained by adding barium dioxide to an ethereal solution of acetic anhydride—

$$2(CH_3{\cdot}CO)_2O + BaO_2 = (CH_3{\cdot}CO)_2O_2 + Ba(CH_3{\cdot}CO_2)_2.$$

It melts at 30° C. and is insoluble in water. It explodes violently when heated, and has the powerful oxidising properties which would be expected from its chemical resemblance to hydrogen peroxide.

363. Corresponding with the thioalcohols, the alkyl sulphides and disulphides (p. 572), there are *thioacids*, *thioanhydrides*, and *thioperoxides*, the oxygen outside the acid radicle, having been exchanged for sulphur in each case.

Thioacetic acid, $CH_3{\cdot}COSH$, is obtained by the action of P_2S_5 on acetic acid:

$$5CH_3{\cdot}COOH + P_2S_5 = 5C_2H_3O{\cdot}SH + P_2O_5.$$

It is a colourless, evil-smelling liquid, boiling at 93° C., and sparingly soluble in water. *Acetyl sulphide* (*thioacetic anhydride*), $(CH_3{\cdot}CO)_2S$, is obtained by the action of P_2S_5 on acetic anhydride, and *acetyl disulphide* (*thioacetic peroxide*), $(CH_3CO)_2S_2$, by the action of K_2S_2 on acetyl chloride.

364. *Propionic acid*, $C_2H_5{\cdot}CO_2H$, is not produced upon a large scale like acetic acid. It is formed in the putrefaction of various organic bodies, and in the destructive distillation of wood and of rosin. It may be separated from formic and acetic acids by saturating the mixture with PbO, evaporating to dryness and extracting with cold water. On boiling the solution, it deposits *basic lead propionate*, leaving the basic lead formate and acetate in solution. From the lead-salt the acid may be obtained by the action of H_2S or H_2SO_4.

Sodium propionate is obtained by the action of CO upon sodium ethoxide, just as sodium formate is obtained from sodium hydroxide (see p. 589)—

$$CO + C_2H_5{\cdot}ONa = C_2H_5{\cdot}CO_2Na.$$

Propionic acid, as would be expected, resembles acetic acid. Its sp. gr. is 0.99, and it boils at 140° C. It has no practical importance. The propionates are mostly soluble in water, but silver propionate is sparingly soluble. Lead propionate is much more difficult to crystallise than lead acetate.

Butyric acid, $C_3H_7{\cdot}CO_2H$. The normal acid (*ethylacetic acid*) is made from cane sugar by dissolving it in water (5 parts), adding a little tartaric acid ($\frac{1}{10}$th part), boiling to convert the sucrose into glucose, and adding to the cooled liquid some putrid cheese ($\frac{1}{15}$th part) rubbed up in about thirty times its weight of milk. Some chalk ($\frac{1}{4}$ part) is stirred into the mixture, which is then allowed to ferment for a week at a temperature of 30°–35° C. The glucose, $C_6H_{12}O_6$, undergoes the *lactic fermentation*, and is converted into lactic acid, $C_3H_6O_3$, which is

converted, by the chalk, into calcium lactate, forming a pasty mass of crystals. After a time the mass becomes liquid again, evolving bubbles of hydrogen and carbon dioxide, and forming a strong solution of calcium butyrate, produced by the *butyric fermentation*. When this is mixed with strong hydrochloric acid, the butyric acid rises to the surface and forms an oily layer, which may be purified by distillation. The passage of lactic acid into butyric acid is expressed by the equation $2C_3H_6O_3 = C_3H_7 \cdot CO_2H + 2CO_2 + 2H_2$.

Butyric acid is a strongly acid liquid, smelling of rancid butter, having the sp. gr. 0.96, and boiling at 163° C. It mixes readily with water, but separates again when the water is saturated with a salt. The butyrates are rather less soluble than the acetates. Calcium butyrate is less soluble in hot water than in cold. Silver butyrate is very sparingly soluble.

Butyric acid is found in the products of distillation of wood and of some other organic bodies. It exists in the perspiration of the skin, and, as a glyceride, in butter, in cod-liver oil, and in some vegetable oils.

Isobutyric acid (*dimethylacetic acid*) $(CH_3)_2CH \cdot COOH$ boils at 155° C. and is made from isopropyl chloride through the cyanide reaction (p. 587).

Valeric or **valerianic acid**. Four of these are possible; that commonly called valeric acid is *isopropylacetic acid*, $(CH_3)_2CH \cdot CH_2 \cdot COOH$. It is prepared by oxidising amyl alcohol (fusel oil) with potassium bichromate and sulphuric acid.

It is an oily liquid smelling like old cheese; its sp. gr. is 0.95, and it boils at 174° C. It is much less soluble in water than are the preceding acids, requiring thirty times its weight. The valerates are, as a rule, easily soluble in water, but the silver salt is sparingly soluble. Zinc valerate is used medicinally.

Valeric acid occurs in valerian root, in the elder, in the berries of the guelder rose, and in many other plants; also in some fish oils and in the perspiration.

Normal caproic or *hexylic acid*, $C_5H_{11} \cdot CO_2H$ (sp. gr. 0.94, b.-p. 205° C.), is found in butter from cows and goats, and in Limburg cheese, being one cause of its odour; it is also found in some plants, and in the perspiration. Caproic acid is formed, together with butyric and acetic acids, in the butyric fermentation described above. It dissolves very sparingly in water, and has a repulsive odour. The caproates of barium and calcium are rather sparingly soluble in water, and silver caproate is nearly insoluble.

365. *Œnanthic* or *normal heptylic acid*, $C_6H_{13} \cdot CO_2H$, is obtained by oxidising œnauthic aldehyde (œnanthol). It has a faint odour and sp. gr. 0.93; it boils at 223° C. Many of the œnanthates are nearly insoluble in water. The strong solutions of the alkali œnanthates become gelatinous on cooling, like solution of soap.

Normal caprylic or *octylic acid*, $C_7H_{15} \cdot CO_2H$, is found in the fusel oil from wines, in old cheese, and, as a glyceride, in butter, human fat, and cocoa-nut oil. It is the first acid of this series which is solid at common temperatures, forming needle-like crystals or scales fusible at 16° C. and boiling at 237°. It has an offensive smell, and is very sparingly soluble in water. The caprylates, except those of the alkalies, are sparingly soluble in water, but they dissolve in alcohol.

Pelargonic or *normal nonylic acid*, $C_8H_{17} \cdot CO_2H$, was originally obtained from the essential oil of *Pelargonium roseum*, and is found among the products of oxidation of oleic acid by nitric acid. It is also formed when essential oil of rue (*nonylmethylketone*) is oxidised by nitric acid. It is an oily liquid, of faint odour, crystallising at 12° C. and boiling at 253°. It has sp. gr. 0.91, and is insoluble in water. The pelargonates are sparingly soluble in water, except those of the alkalies.

Lauric or *normal dodecylic acid*, $C_{11}H_{23} \cdot CO_2H$, is obtained from a fatty substance found in the fruit of the sweet bay (*Laurus nobilis*) and in *sassafras-nuts* or *pichurim beans*, which are used for flavouring chocolate, and are the seeds of another of the Lauraceæ (*Nectandra Puchury*). A similar substance is found in the mango and in a variety of cochineal insect. The fat is saponified by boiling with potash, the solution decomposed by hydrochloric acid, and the separated fatty acid distilled, when lauric acid is found in the first fractions.

The crystals of lauric acid fuse at 44° C. It cannot be distilled at ordinary pressures without decomposition.

366. Palmitic acid, $C_{15}H_{31} \cdot CO_2H$, crystallises in needles (m.-p. 62° C.), and is the first of the *fatty acids*, properly so called, which occur as glycerides in the vegetable and animal fats, and form true *soaps* with

the alkalies, such soaps being the salts formed by the fatty acid with the alkali-metal, characterised by easily *lathering* when dissolved in soft water, by being precipitated from their aqueous solutions by common salt, and by giving an oily layer of the melted fatty acid when boiled with any of the common acids.

On the large scale, palmitic acid is made from palm-oil, as described at p. 576. It is also manufactured by heating oleic acid with caustic soda:

$$C_{17}H_{33}\cdot COOH + 2NaOH = C_{15}H_{31}\cdot COONa + CH_3\cdot COONa + H_2.$$

On the small scale, palm-oil is boiled with potash, which converts it into potassium palmitate and oleate; on adding dil. H_2SO_4 to the solution, a mixture of

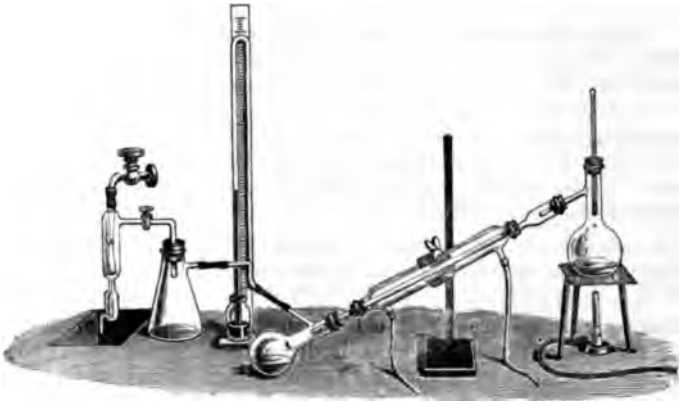


Fig. 273. Distillation under diminished pressure.

palmitic and oleic acids is precipitated; this is washed, dried, and dissolved in hot alcohol, from which the palmitic acid crystallises on cooling, leaving the oleic acid in solution. It may be purified by distillation under diminished pressure. An arrangement suitable for this operation is shown in Fig. 273. Palm-oil contains the glycerides *palmitin* and *olein*, which are *saponified* by the potash, with liberation of glycerine, as will be further explained under the head of *Ethereal salts*, to which the glycerides belong.

The substance known as *adipocere*, a wax-like mass left when animal bodies decompose in the earth, is a mixture of palmitates of calcium and potasium.

The formation of palmitic acid from spermaceti has been explained at p. 570.

Stearic acid, $C_{17}H_{35}\cdot CO_2H$, may be prepared from suet by boiling it with potash, decomposing with hydrochloric acid the soap thus obtained, drying the separated fatty acids, and dissolving in the least possible quantity of hot alcohol. This retains the oleic acid in solution and deposits a mixture of stearic and palmitic acids on cooling; the mixture is well pressed in blotting-paper, and repeatedly crystallised from alcohol till it fuses at 69° C. The stearic acid exists in the suet and in most other solid fats, in the form of the glyceride *stearin*, mixed with palmitin and a little olein. When saponified by the potash, these yield the stearate, palmitate, and oleate of potassium, respectively.

Stearic acid is a white crystalline solid, of the same sp. gr. as water, fusing at 69° C., and not distilling without partial decomposition, except at low pressures or in a current of superheated steam. It is insoluble in

water, but dissolves in alcohol and in ether. It burns with a luminous flame. The alkalies dissolve stearic acid on heating, forming stearates, which are components of ordinary soaps.

White curd soap made from tallow and soda consists chiefly of *sodium stearate*, $C_{17}H_{35}\cdot CO_2Na$, which may be crystallised from alcohol. It dissolves in a little water to a clear solution, but when this is largely diluted it deposits scaly crystals of the *acid sodium stearate*, $(C_{17}H_{35}\cdot CO_2)_2HNa$. Potassium stearate behaves in a similar way. The other stearates are insoluble. Those of calcium and magnesium are precipitated when hard water is brought in contact with soap. Magnesium stearate may be crystallised from alcohol.

Stearic acid mixed with palmitic acid is the material of the so-called *stearin candles*.

Margaric acid, $C_{16}H_{33}\cdot CO_2H$, is obtained by boiling cetyl cyanide with an alkali. It crystallises like palmitic, and fuses at 60° C.

367. **Acids from Monohydric Olefine Alcohols (Acrylic or Oleic Series).**—These correspond with the general formula $C_nH_{2n-1}COOH$ and contain the ethylenic linking characteristic of the olefines, *e.g.*, $CH_3\cdot CH : CH\cdot COOH$, crotonic acid. They may be prepared from the corresponding alcohols and cyanogen derivatives by the general methods (p. 587), and also by two methods which recall the preparation of the olefines. These are (1) by nuclear condensation from the monohalogen substituted fatty acids, thus:

$$CH_3\cdot CH_2\cdot CHCl\cdot COOH + KOH = CH_3\cdot CH : CH\cdot COOH + KCl + HOH,$$

and (2) by dehydration of the alcohol acids (p. 574) by destructive distillation; $CH_2(OH)\cdot CH_2\cdot CH_2\cdot COOH = CH_2 : CH\cdot CH_2\cdot COOH + HOH$.

Attention must here be called to the nomenclature of isomerides among derivatives of open-chain hydrocarbons. The letters, α, β, γ, &c., are prefixed to the name of the derivative to indicate the carbon atom to which the substituent is attached, α signifying the atom next the end characteristic group, β the next but one, γ the next but two, and so on, thus:

α-Chlorobutyric acid = $CH_3\cdot CH_2\cdot CHCl\cdot COOH$
β-Chlorobutyric acid = $CH_3\cdot CHCl\cdot CH_2\cdot COOH$
γ-Chlorobutyric acid = $CH_2Cl\cdot CH_2\cdot CH_2\cdot COOH$

It is by no means a matter of indifference whether an α, β, or γ derivative is used in the two last named reactions; in both cases the β-derivative is most easily converted into the acid of the olefine series.

Having an ethylenic linking, the acids of the acrylic series show the property, characteristic of the olefines, of combining directly with two atoms of bromine and with two atoms of (nascent) hydrogen. In the former case a dibromo-derivative of the corresponding fatty acid, and in the latter the fatty acid itself, is formed, the double linking being opened up in each case.

A characteristic reaction of the acids of this series is that when fused with an alkali they yield alkali salts of two acids of the acetic series, the rupture of the molecule generally occurring at the double linking; thus acrylic acid, $CH_2 : CH\cdot COOH$ yields acetate and formate, and crotonic acid yields two molecules of acetate.

This reaction is not a criterion of the position of the double linking in the chain because of the influence which alkalies have in causing the double bond to shift, mere heating with aqueous alkali sufficing in many cases to convert a $\beta\gamma$-acid (one in which the double bond is between the β and γ carbon atom) into an $\alpha\beta$-acid.

Isomerism among acids of the acrylic series may be due to variation in position of the double bonds, as, for instance, $CH_3\cdot CH : CH\cdot CH_2\cdot COOH$ and $CH_3\cdot CH_2\cdot CH : CH\cdot COOH$

or to the substitution of a hydrocarbon radicle for H, *e.g.*, $CH_3 \cdot CH : C(CH_3) \cdot COOH$, isomeric with the two preceding acids.

There are also cases of stereoisomerism of the same kind as that between fumaric and malæic acids (*q.v.*).

Since the polymethylenes (p. 539) are isomeric with the olefines, the monocarboxylic acids derived from them are isomeric with the acrylic acids, though they do not belong to the same series.

The following are the best-known acids of the series, but although they form an homologous series, many of them differ in structure so much from the type, acrylic acid, and from each other that their physical properties cannot advantageously be compared.

Acid.	Source.	Formula.
Acrylic	Oxidation of acrolein	$C_2H_3 \cdot CO_2H$
Crotonic		$C_3H_5 \cdot CO_2H$
Angelic	Angelica root	$C_4H_7 \cdot CO_2H$
Pyroterebic	Oxidation of turpentine	$C_5H_9 \cdot CO_2H$
Hypogaeic	Earth-nut oil	$C_{15}H_{29} \cdot CO_2H$
Oleic	Most oils	$C_{17}H_{33} \cdot CO_2H$
Erucic	Rape oil	$C_{21}H_{41} \cdot CO_2H$

Acrylic acid, $CH_2 : CH \cdot CO_2H$, is obtained by heating acrolein, the corresponding aldehyde, (p. 583) with water and silver oxide in the dark : $C_2H_3 \cdot CHO + Ag_2O = C_2H_3 \cdot CO_2H + Ag_2$. It is also obtained, by the general methods given above, from bromopropionic and hydroxypropionic acids. It is a pungent liquid, miscible with water, and boiling at 140° C. Nascent hydrogen converts it into propionic acid, $C_2H_5 \cdot CO_2H$. Fused with potassium hydroxide, it yields potassium acetate and formate—$CH_2 : CH \cdot CO_2K + KOH + H_2O = CH_3 \cdot CO_2K + H \cdot CO_2K + H_2$.

While it is possible to write the formula $C_3H_5 \cdot COOH$, the next homologue to acrylic acid, in four isomeric forms, two alone are known with certainty viz., *crotonic acid*, $CH_3 \cdot CH : CH \cdot COOH$, which occurs in a solid and a liquid modification, and *methylacrylic acid*, $CH_2 : C(CH_3) \cdot COOH$. *Vinylacetic acid*, $CH_2 : CH \cdot CH_2 \cdot COOH$, is also alleged to have been obtained.

Solid crotonic acid occurs in crude pyroligneous acid, and is obtained by oxidation of croton adelhyde (p. 584) with Ag_2O. Its formation by heating *αβ*-dibromobutyric acid with KI solution indicates the position of the double linking:

$$CH_3 \cdot CHBr \cdot CHBr \cdot COOH + 2KI = CH_3 \cdot CH : CH \cdot COOH + 2KBr + I_2.$$

It crystallises in needles, melts at 72° C., and boils at 180° C., its vapour condensing in plates. It is moderately soluble in water, and has an odour like that of butyric acid, into which it is converted by nascent hydrogen. Fused KOH converts it into potassium acetate—$C_3H_5 \cdot CO_2H + 2KOH = 2(CH_3CO_2K) + H_2$. *"Liquid" crotonic* or *isocrotonic acid* occurs in croton oil. When PCl_5 acts on ethylacetoacetate (*q.v.*) it produces *β*-chloroisocrotonic acid, $CH_2 \cdot CCl : CH \cdot CO_2H$, which, by treatment with nascent H, yields isocrotonic acid ; this crystallises in needles or prisms, melts at 15° C., boils at 169° C., and is converted into the solid acid at 180° C. It appears to be a stereoisomeride of the solid acid, the relation between the two being similar to that between fumaric and malæic acids (*q.v.*). *Methylacrylic acid* occurs in chamomile oil, and has an odour of mushrooms. It is prepared by a complicated process. It melts at 16° C. and boils at 160° C. ; nascent H converts it into isobutyric acid, whilst with fused KOH it yields propionate and formate.

Angelic acid, $CH_3 \cdot CH : C(CH_3) \cdot COOH$, is obtained by boiling angelica root (an umbelliferous plant) with lime and water, filtering, acidifying with sulphuric acid, and distilling. The acid appears to be contained in the root as an ethereal salt, which is decomposed by the lime. Chamomile flowers and some other aromatic plants also yield this acid. It crystallises in prisms, fusing at 45° C., and boiling at 185°. It has an aromatic odour, is soluble in hot water and in alcohol and ether. When boiled for some time, it is converted into its stereoisomeride, *tiglic acid* (m.-p. 64° C., b.-p. 198° C.), which is also obtained from croton oil (*Croton tiglium*), and, together with angelic acid, from cummin oil (*Cuminum cyminum*). Fused with KOH, angelic acid yields acetate and propionate. There are several isomerides.

368. **Oleic acid,** $C_{17}H_{33}\cdot CO_2H$, or $C_8H_{17}\cdot CH:CH[CH_2]_7\cdot COOH$, the most important member of the acrylic series of acids, is prepared by boiling olive-oil with potash, and decomposing the solution with hydrochloric acid, which separates the oleic acid as an oily layer, containing some stearic and palmitic acids. To purify it, it is heated with litharge at 100° C. for some hours, when a mixture of oleate, palmitate, and stearate of lead is obtained. The oleate is extracted from this mixture by ether, and the solution shaken with HCl, which precipitates the lead as $PbCl_2$, while the oleic acid remains dissolved in the ether, which rises to the surface. The ether is distilled off and the oleic acid is purified by fractional distillation under diminished pressure.

The olive-oil contains the glyceride *olein*, which is decomposed by boiling with potash into glycerine and potassium oleate. Olein is a general constituent of the fixed oils; the *soft soap* made by saponifying whale and seal oils with potash consists chiefly of potassium oleate. Oleic acid is a by-product in the manufacture of candles, in which its presence would be injurious by lowering the fusing-point. It is used in greasing wool for spinning, being much more easily removed by alkalies than is olive-oil, which was formerly employed. Ammonium oleate is sometimes employed as a mordant for the aniline dyes on cotton.

Oleic acid is an oily liquid which crystallises at 0° C. and melts at 14°. When distilled, it yields a number of products of decomposition, among which *sebacic acid*, $C_8H_{16}(CO_2H)_2$, is conspicuous. In a current of superheated steam, at 250° C., it may be distilled without decomposition. In its commonly impure state, it absorbs oxygen readily when exposed to air.

Fusion with KOH converts oleic acid into acetate and palmitate (see p. 596).

The constitution of oleic acid follows from the fact that when treated with Br it yields a dibromostearic acid, which is converted by alcoholic potash into *stearolic acid* containing a treble linking. By oxidation stearolic acid yields two acids, each containing C_9; as acids from acetylene alcohols break up on oxidation at the treble linking, stearolic acid, must contain that linking between the ninth and tenth C atoms, and this must also be the position of the double bond in oleic acid.

By the action of N_2O_3, oleic acid is converted into the isomeric *elaidic acid*, which is crystalline, and fuses at 51° C. When oxidised by nitric acid, oleic acid yields several acids of the acetic and oxalic series. When heated with amorphous phosphorus and strong hydriodic acid at about 200° C., it yields stearic acid, $C_{17}H_{35}\cdot CO_2H$.

The alkali oleates are decomposed by much water into free alkalies and insoluble acid oleates. *Sodium oleate* is present in ordinary soap, and may be crystallised from absolute alcohol.

Barium oleate is a crystalline powder, insoluble in water, and sparingly soluble in boiling alcohol. *Lead oleate*, which forms the chief part of *lead plaster*, fuses at 80° C., and solidifies on cooling to a translucent brittle mass, soluble in ether.

Erucic acid, $C_8H_{17}\cdot CH:CH[CH_2]_{11}\cdot COOH$ occurs as a glyceride in rape oil and in the fatty oils of mustard and grape seed. It fuses at 34° C. When heated with phosphorus and hydriodic acid, it gives behenic acid, $C_{21}H_{43}\cdot CO_2H$. Heating with HNO_3 dil. converts it into the isomeride *brassidic acid* (m.-p. 66° C.).

369. **Acids from Monohydric Acetylene Alcohols.—Acids of the general form, $C_nH_{2n-3}COOH$, may be acetylene derivatives, containing trebly linked carbon atoms, or diolefine derivatives, containing two doubly linked carbon atoms.**

The acetylene acids are obtained from the acids of the oleic series by combining them with two atoms of Br to form dibromacetic acids and treating the products with alcoholic potash; thus, $\alpha\beta$-dibromopropionic acid yields propiolic acid—

$$CH_2Br\cdot CHBr\cdot COOH + 2KOH = CH \vdots C\cdot COOH + 2KBr + 2HOH.$$

They are also obtained by heating monohalogen substituted oleic acids with alkali—

$$CH_2 : CBr\cdot COOH + KOH = CH \vdots C\cdot COOH + KBr + HOH.$$

These methods should be compared with those for obtaining acetylenes.

Another method consists in heating the alkali acetylides with CO_2—

$$CH_3 \vdots CNa + CO_2 = CH_3C \vdots C\cdot COONa.$$

Like the acetylenes, these acids combine with two or four atoms of Br or other monovalent element, and those which contain the group $\cdot C \vdots CH$ yield explosive metallic derivatives (p. 538).

370. *Propiolic acid*, $CH \vdots C\cdot CO_2H$, corresponding with propargyl alcohol, is prepared, as its potassium salt, by heating potassium hydrogen acetylene-dicarboxylate in aqueous solution ;

$$CO_2H\cdot C \vdots C\cdot CO_2K = CO_2 + HC \vdots C\cdot CO_2K.$$

It melts at 6° C., boils at 144° C., and yields explosive metallic derivatives. Just as acetylene polymerises to benzene (p. 538), so propiolic acid polymerises (in sunlight) to trimesic acid, $C_6H_3(COOH)_3$

Tetrolic acid, $C_3H_3\cdot CO_2H$, has no practical importance. It is produced when β-chlorocrotonic acid is heated at 100° C. with alcoholic potash. It is also formed by heating sodium allylide in carbon dioxide ; m.-p. 76°, b.-p. 203° C.

Sorbic acid, $CH_3\cdot CH : CH\cdot CH : CH\cdot COOH$, is a diolefinic acid, produced by boiling with acid or alkali the yellow fragrant oil obtained by distilling the juice of unripe mountain-ash berries (*Sorbus*). By oxidation with $K_2Mn_2O_8$ it yields aldehyde and tartaric acid.

Sorbic acid fuses at 134°.5 C., and is decomposed when distilled, unless in presence of steam. It is sparingly soluble in water, but dissolves in alcohol.

Linoleic acid, $C_{17}H_{31}\cdot COOH$, occurs as a glyceride in linseed oil and some other drying oils. The oil is saponified with KOH, the aqueous solution is precipitated by $CaCl_2$ and the calcium linoleate extracted by ether. It is a yellowish oil, not altered by N_2O_3. *Palmitolic acid* is an isomeride. *Homolinoleic* acid and *stearolic* acid, $C_8H_{17}\cdot C \vdots C[CH_2]_7\cdot COOH$, are also isomerides.

Linolenic and *isolinolenic acids* are isomerides of the formula $C_{18}H_{30}O_2$, belonging to the $C_nH_{2n-5}\cdot CO_2H$ series of acids. They occur as glycerides in linseed oil and other drying oils.

371. **Acids from Monohydric Aromatic Alcohols (Aromatic or Benzoic Series).**—These may be of two kinds :

(1) Acids containing the COOH group attached to the benzene nucleus, such as *benzoic acid*, $C_6H_5\cdot COOH$, and *toluic acid*, $C_6H_4(CH_3)\cdot COOH$. These are obtainable (*a*) by oxidising the hydrocarbons containing side-chains (p. 548), (*b*) by oxidising the corresponding alcohols or aldehydes, (*c*) by the action of sodium and carbon dioxide on the monohalogen substituted hydrocarbons—$C_6H_5Br + CO_2 + Na_2 = C_6H_5COONa + NaBr$, (*d*) by fusing the alkali salts of the sulphonic acids (p. 648) with alkali formate — $C_6H_5SO_3Na + HCOONa = C_6H_5COONa + NaHSO_3$, (*e*) by hydrolysis of the cyanogen substitution products of the hydrocarbons—$C_6H_5CN + 2HOH = C_6H_5COOH + NH_3$.

(2) Acids containing the COOH group as part of the side-chain ; these may be regarded as open-chain acids in which aromatic radicles (C_6H_5; $C_6H_4(CH_3)$, &c.) have been substituted for H, as in *phenylacetic acid*, $C_6H_5\cdot CH_2\cdot COOH$, and *tolylacetic acid*, $C_6H_4(CH_3)\cdot CH_2\cdot COOH$. They may be prepared by hydrolysis of the corresponding cyanogen derivatives—$C_6H_5\cdot CH_2\cdot CN + 2HOH = C_6H_5\cdot CH_2\cdot COOH + NH_3$.

The aromatic acids are crystalline, volatile, sparingly soluble in water, but soluble in alcohol and ether. They show most of the reactions of the fatty acids, and like them are converted into hydrocarbons when heated with lime, which abstracts CO_2.

372. **Benzoic acid,** $C_6H_5{\cdot}CO_2H$ (*phenyl formic acid*). This acid was originally extracted from *gum benzoin*, a resinous exudation from *Styrax benzoin*, a tree of the Malay Islands.

When the gum is gently heated in an iron or earthen vessel, covered with perforated paper and surmounted by a drum of paper, the benzoic acid, which exists uncombined in the resin, rises as vapour and condenses in the drum. A better yield is obtained by boiling the benzoin with lime and water, and decomposing the filtered solution of calcium benzoate with hydrochloric acid.

It is also made from the urine of cows and horses, which contains hippuric acid, easily convertible into benzoic acid (see *Hippuric acid*).

But the chief source of modern benzoic acid is toluene, $C_6H_5{\cdot}CH_3$. This is directly convertible into benzoic acid by oxidation with nitric acid, $C_6H_5{\cdot}CH_3 + 2HNO_3 = C_6H_5{\cdot}CO_2H + 2HOH + 2NO$.

It is cheaper, however, to convert the toluene into benzo-trichloride by passing chlorine into it at 180° C., and to heat the product with lime; $C_6H_5{\cdot}CH_3 + Cl_6 = C_6H_5{\cdot}CCl_3 + 3HCl$; $2C_6H_5Cl_3 + 4Ca(OH)_2 = 3CaCl_2 + (C_6H_5{\cdot}CO_2)_2Ca + 4HOH$. The calcium benzoate is decomposed by hydrochloric acid, when benzoic acid separates.

Much benzoic acid is obtained as a by-product in making benzaldehyde from toluene (p. 584), for much of the benzaldehyde is converted into benzyl alcohol and calcium benzoate by the excess of lime used (p. 585).

Benzene, C_6H_6, may be partly converted into benzoic acid by oxidising it with MnO_2 and H_2SO_4. Addition of formic acid increases the yield of benzoic acid; $C_6H_6 + H{\cdot}CO_2H + O = C_6H_5{\cdot}CO_2H + H_2O$.

Properties of benzoic acid.—It crystallises in shining needles or in feathery scales, usually having a faint aromatic odour. It fuses at 120° C. and boils at 250° C., subliming without decomposition; it volatilises when boiled with water. It is sparingly soluble in cold water (200 parts), more easily in hot water (24 parts); alcohol and ether dissolve it readily. Potash and ammonia also dissolve it immediately, and it is precipitated on adding an acid. Most of the benzoates are soluble, but *ferric benzoate* is obtained as a buff-coloured precipitate when ferric chloride is added to a neutral benzoate.

By distillation with excess of lime, benzoic acid yields benzene—

$$C_6H_5{\cdot}CO_2H + CaO = CaCO_3 + C_6H_6.$$

When vapour of benzoic acid is passed over heated zinc-dust, it is converted into bitter-almond oil (benzoic aldehyde)—

$$C_6H_5{\cdot}CO_2H + Zn = C_6H_5{\cdot}CHO + ZnO.$$

By boiling with strong HNO_3, benzoic acid is converted into nitrobenzoic acids, $C_6H_4(NO_2){\cdot}CO_2H$, of which three exist.

By distilling benzoic acid with PCl_5, *benzoyl chloride* is obtained; $C_6H_5{\cdot}COOH + PCl_5 = C_6H_5{\cdot}COCl + POCl_3 + HCl$. This chloride bears the same relation to benzoic acid as acetyl chloride bears to acetic acid, the radicles benzoyl and acetyl being related in a similar way to benzyl and ethyl:

Ethyl, $CH_3{\cdot}CH_2$; Acetyl, $CH_3{\cdot}CO$	Benzyl, $C_6H_5{\cdot}CH_2$; Benzoyl, $C_6H_5{\cdot}CO$
Ethyl hydride (ethane), $CH_3{\cdot}CH_3$	Benzyl hydride (toluene), $C_6H_5{\cdot}CH_3$
Ethyl hydroxide (alcohol), $CH_3{\cdot}CH_2{\cdot}OH$	Benzyl hydroxide, $C_6H_5{\cdot}CH_2OH$
Acetyl hydride (aldehyde), $CH_3{\cdot}COH$	Benzoyl hydride, $C_6H_5{\cdot}COH$
Acetyl hydroxide (acetic acid), $CH_3{\cdot}COOH$	Benzoyl hydroxide, $C_6H_5{\cdot}COOH$

373. *Benzoic anhydride*, or *dibenzoyl oxide*, $(C_6H_5\cdot CO)_2O$, is produced by heating benzoyl chloride with dry sodium benzoate—

$$C_6H_5\cdot COCl + C_6H_5\cdot COONa = (C_6H_5\cdot CO)_2O + NaCl.$$

The mass is washed with water and the anhydride crystallised from alcohol. It fuses at 42° C. and boils at 360° C. Boiling with water converts it slowly into benzoic acid.

By heating benzoyl chloride with dry sodium acetate, *benzoacetic anhydride* is obtained; $C_6H_5\cdot COCl + CH_3\cdot COONa = (C_6H_5\cdot CO)(CH_3\cdot CO)O + NaCl$.

Benzoic peroxide $(C_6H_5\cdot CO)_2O_2$, is obtained by acting on benzoyl chloride with barium dioxide; $2C_6H_5\cdot COCl + BaO_2 = (C_6H_5\cdot CO)_2O_2 + BaCl_2$. It may be crystallised from ether. Like hydrogen peroxide, it is decomposed explosively when moderately heated. Alkalies resolve it into benzoic acid and oxygen.

374. **Toluic acids**, or *methyl-benzoic acids*, $C_6H_4(CH_3)\cdot CO_2H$, are obtained by oxidising the three xylenes, $C_6H_4(CH_3)_2$, with dilute nitric acid. The 1 : 2-acid crystallises in needles, fusing at 102° C., and is sparingly soluble in water.

Mesitylenic acid, $1:3:5-C_6H_3(CH_3)_2\cdot CO_2H$, is prepared by oxidising mesitylene, (p. 549), with dilute nitric acid. It is a crystalline volatile acid, fusing at 166° C. and soluble in boiling water and in alcohol.

Cuminic or *isopropyl-benzoic acid*, $1:4-C_6H_4(C_3H_7)\cdot CO_2H$, is prepared from the aldehyde existing in Roman cummin oil, by boiling it with alcoholic solution of potash, which converts it into cuminic alcohol and potassium cuminate. On adding an acid to the aqueous solution of potassium cuminate, the cuminic acid is precipitated, and may be crystallised from alcohol; it fuses at 116° C., and may be sublimed.

375. **Phenylolefinecarboxylic acids** are those in which the COOH group occurs in an unsaturated side-chain (p. 549).

Cinnamic or *β-phenyl-acrylic acid*, $C_6H_5\cdot CH : CH\cdot CO_2H$, is prepared by boiling storax with soda, and decomposing the solution of sodium cinnamate with HCl, which precipitates the cinnamic acid in feathery crystals like benzoic acid, fusing at 133° C., boiling at 300°, and subliming undecomposed. It is soluble in boiling water and in alcohol.

Its connection with acrylic acid is shown by fusing it with potash, which yields acetate and benzoate of potassium, whilst acrylic acid yields acetate and formate; $C_6H_5\cdot CH : CH\cdot CO_2H + 2KOH = CH_3\cdot CO_2K + C_6H_5\cdot CO_2K + H_2$.

Oxidising agents convert cinnamic acid into benzoic aldehyde (bitter-almond oil); $C_6H_5\cdot CH : CH\cdot CO_2H + O_4 = C_6H_5\cdot CHO + 2CO_2 + H_2O$. When distilled with excess of lime, it yields *cinnamene* or *phenyl-ethylene* (p. 550).

Nascent hydrogen converts it into *β-phenyl-propionic acid* or *hydrocinnamic acid*;

$$C_6H_5\cdot CH : CH\cdot CO_2H + H_2 = C_6H_5\cdot CH_2\cdot CH_2\cdot CO_2H.$$

Cinnamic acid may be obtained synthetically by the action of sodium acetate on bitter-almond oil, in presence of acetic anhydride, which probably acts as a dehydrating agent; $CH_3\cdot CO_2Na + C_6H_5\cdot CHO = C_6H_5\cdot CH : CH\cdot CO_2Na + H_2O$; and by heating benzal chloride with sodium acetate—

$$C_6H_5\cdot CHCl_2 + CH_3\cdot COONa = C_6H_5\cdot CH : CH\cdot COONa + 2HCl.$$

Atropic acid, *α-phenyl-acrylic acid*, $C_6H_5\cdot C\begin{matrix}\diagup COOH\\ \diagdown CH_2\end{matrix}$, is produced when atropine, the alkaloid of deadly nightshade, is boiled with baryta or with HCl. It fuses at 106° C.

The **napthoic acids** (α and β), $C_{10}H_7\cdot CO_2H$, are monocarboxylic naphthalenes, obtained by the hydrolysis of the corresponding cyanogen derivatives.

376. **Monobasic Acids from Polyhydric Alcohols.**—As already noticed (p. 574), these acids may be alcohol-acids, or aldehyde-acids if the polyatomic alcohol be a glycol, and keto-acids, or even keto-alcohol- or keto-aldehyde-acids, if the alcohol be polyhydric, in which case it must contain both primary and secondary alcohol groups.

Alcohol-acids are termed *hydroxy-acids*, a title which is warranted by the fact that they can be prepared from the chloro-substituted open-chain acids of the foregoing series by treatment with silver oxide and water, showing that OH has been substituted for the Cl, as, for

instance, when monochloracetic acid is converted into glycollic acid; $CH_2Cl{\cdot}COOH + AgOH = CHOH{\cdot}COOH + AgCl$.

It will be found that the hydrogen of the hydroxyl group in a hydroxy-acid can be exchanged for a metal, just as it is in the hydroxyl group of an alcohol, so that the acid possesses the functions of both an alcohol and an acid. Thus, the monobasic hydroxy-acids may contain two or more H atoms, which can be exchanged for a metal, although they are strictly monobasic, since they contain only one CO_2H group; hence they are sometimes termed *diatomic* (*triatomic*, *&c.*) *monobasic acids*.

Besides the treatment of the monohalogen substituted fatty acids with silver oxide or alkali, referred to above, there is a number of other methods available for preparing hydroxy-acids. One of these is, of course, the oxidation of the polyhydric alcohols; another is the oxidation of fatty acids containing the group R_2CH, such as *isobutyric acid*, $(CH_3)_2CH{\cdot}COOH$, which yields *hydroxyisobutyric acid*, $(CH_3)_2C(OH){\cdot}COOH$, when oxidised with alkaline permanganate. Or the olefine acids may be converted by hydrolysis into hydroxy-acids, $CH : CH{\cdot}COOH + H_2O = CH_2{\cdot}CH(OH){\cdot}COOH$. Again, the amido-acids may be treated with nitrous acid, $CH_2(NH_2){\cdot}COOH$ (amido-acetic acid) $+ NO{\cdot}OH = CH_2(OH){\cdot}COOH + N_2 + H_2O$ (*cf.* p. 105). The general method of hydrolysing cyanogen derivatives is also available; thus the aldehydes, when treated with HCN, yield cyanohydrins, such as $CH_3{\cdot}CH(OH){\cdot}CN$, and these may be hydrolysed to acids (p. 587).

The simplest hydroxy-acid, *hydroxy-formic acid*, $HO{\cdot}COOH$, would be the first anhydride of orthocarbonic acid (p. 261), carbon monoxide being the second anhydride. It does not exist, probably for the reason already given (p. 573), but if it did it might be identical with carbonic acid.

When copper sulphate solution is added to a strong solution of potassium carbonate, a deep blue solution is obtained which is similar to, although less stable than, the solutions obtained by adding copper sulphate to other hydroxy-acids. This supports the supposition that carbonic acid is hydroxy-formic acid.

Glycollic or hydroxyacetic acid, $CH_2OH{\cdot}CO_2H$, is a product of the oxidation of glycol, $CH_2OH{\cdot}CH_2OH$, by dil. HNO_3, but is best prepared by the careful oxidation of alcohol by nitric acid.

Into a narrow glass cylinder (2 inches in diameter) pour 118 cubic centimetres of 80 per cent. alcohol; insert a funnel tube drawn out to a fine opening, to the bottom of the vessel, and pour in 50 c.c. of water, so as to form a layer below the alcohol; then pour in carefully through the funnel 126 c.c. of nitric acid of sp. gr. 1.35, to form a layer below the water. Place the vessel aside, without shaking, for about five days at about 20° C., when the three layers will have mixed. Evaporate the liquid upon the water-bath, in separate portions of about 20 c.c. to a syrup, dilute it with 10 volumes of water, boil, and neutralise with powdered chalk. To the crystalline paste which forms on cooling, add an equal bulk of alcohol, and filter. The precipitate is boiled with water, and filtered while boiling, from undissolved calcium oxalate. On cooling, it deposits calcium glyoxylate, whilst calcium glycollate remains in solution; this is boiled with a little lime to decompose any glyoxylate, and the filtered solution evaporated and treated with enough oxalic acid to precipitate the calcium as oxalate, leaving glycollic acid in solution.

The action of nitric acid upon alcohol is of a representative character. The groups CH_3 and $CH_2{\cdot}OH$, contained in ethyl alcohol, are converted under the influence of oxidising-agents into CHO, characteristic of the

aldehydes, and COOH, characteristic of the acids respectively. Accordingly, we find, among the products of the oxidation by nitric acid, acetic aldehyde, $CH_3{\cdot}CHO$; acetic acid, $CH_3{\cdot}COOH$; glyoxal, $CHO{\cdot}CHO$; glyoxylic acid, $CHO{\cdot}COOH$; glycollic acid, $CH_2{\cdot}OH{\cdot}COOH$; and oxalic acid, $COOH{\cdot}COOH$.

Glycollic acid has been obtained by allowing the vinegar ferment, *bacterium aceti*, to grow in a dilute solution of glycol (ethene-alcohol).

Properties of glycollic acid.—Crystallises with some difficulty; fuses at 80° C., and volatilises slowly at 100°. Very soluble in water, alcohol, and ether.

As might be expected, oxidising-agents convert it into oxalic acid, from which it may be obtained by reduction. When heated with sulphuric acid it yields formic aldehyde and formic acid; $CH_2OH{\cdot}CO_2H = H{\cdot}CHO + H{\cdot}CO_2H$. The formic aldehyde is converted into formic paraldehyde, $(HCOH)_3$, and most of the formic acid is decomposed in H_2O and CO.

When glycollic acid is heated with HCl it yields chloracetic acid; $CH_2OH{\cdot}CO_2H + HCl = CH_2Cl{\cdot}CO_2H + H_2O$. With PCl_5 it yields chloracetyl chloride, $CH_2Cl{\cdot}COCl$.

Hydriodic acid reduces glycollic to acetic acid—

$$CH_2OH{\cdot}CO_2H + 2HI = CH_3{\cdot}CO_2H + H_2O + I_2.$$

The glycollates of calcium, copper, and silver are sparingly soluble in cold water but dissolve in boiling water.

Glycollic acid occurs in unripe grapes, and in the leaves of the Virginia creeper. It can be made from glucose by oxidising it with silver oxide, in the presence of calcium carbonate to keep the solution neutral, or else the glycollic acid becomes oxalic acid.

377. **Lactic acids** or *hydroxypropionic acids*, $C_2H_4(OH){\cdot}CO_2H$.—Since propionic acid is $CH_3{\cdot}CH_2{\cdot}COOH$, there can be two hydroxypropionic acids, viz., the α-acid, $CH_3{\cdot}CHOH{\cdot}COOH$, and the β-acid, $CH_2OH{\cdot}CH_2{\cdot}COOH$; the former is called *ethylidene lactic acid*, and the latter *ethylene lactic acid*.

Ethylidene lactic acid, $CH_3{\cdot}CHOH{\cdot}COOH$, is also known as *fermentation lactic acid*, being the acid of sour milk produced by the fermentation of the milk sugar by the lactic bacillus. As pointed out at p. 593, glucose also undergoes this fermentation, the source of the bacillus in that case being putrid cheese; the chemical change is expressed by the equation $C_6H_{12}O_6 = 2C_3H_6O_3$.

On a large scale a mash of starchy material, such as maize, is treated with malt to convert the starch into maltose, and is then mixed with a cultivation of the bacillus, chalk being stirred in for the purpose of neutralising the lactic acid as it is formed, lest it kill the bacillus. The most favourable temperature is about 50° C. When all the maltose has been converted, the solution of calcium lactate is treated with sulphuric acid, the precipitated $CaSO_4$ is filtered off, and the dilute lactic acid is concentrated in a vacuum pan to a strength of about 50 per cent., in which form it is sold for use as a mordant and as an addition to the tanning liquors in leather factories.

Pure lactic acid, obtained by decomposing zinc lactate with H_2S, is a colourless, strongly acid liquid which crystallises when cooled and then melts at 18° C. It can be distilled at 120° C. under 12 mm. pressure, but at higher temperatures it loses water, yielding a much more stable compound, *lactide*, $O\begin{<}\begin{matrix}CH(CH_3)CO\\CO(CH_3)CH\end{matrix}\end{>}O$, which melts at 125° C. and boils at 255° C.

It is characteristic of the α-alcohol acids that they yield anhydrides from two molecules by the loss of water derived from the alcoholic groups or from the carboxylic groups, or from both. Thus from two molecules of glycollic acid may be obtained, by loss of one molecule of water, $COOH{\cdot}CH_2-O-CH_2COOH$ (*diglycollic acid*), $CH_2OH{\cdot}CO-O-CO{\cdot}CH_2OH$ (not known), or $CH_2OH{\cdot}CO-O-CH_2{\cdot}COOH$ (*glycolglycollic acid*, an ethereal salt formed from the *acid* glycollic acid and the *alcohol* glycollic acid). If the first and second of these lose another mol. H_2O the same compound will be formed, namely $O\langle^{CH_2{\cdot}CO}_{CH_2{\cdot}CO}\rangle O$ (*diglycollic anhydride*); from the third, the subtraction of another mol. H_2O yields *glycolide*, $O\langle^{CH_2{\cdot}CO}_{CO{\cdot}CH_2}\rangle O$, of which lactide is a homologue.

Ethylidene lactic acid is found in the gastric juice, and in opium.

When lactic acid is heated at 130° C. with dilute sulphuric acid, in a sealed tube, it yields aldehyde and formic acid; $C_2H_5O{\cdot}CO_2H = CH_3{\cdot}CHO + H{\cdot}CO_2H$. Oxidation with $K_2Mn_2O_8$ converts this lactic acid into the ketonic acid, *pyruvic acid*, $CH_3{\cdot}CO{\cdot}COOH$. This is only to be expected, since ethylidene lactic acid contains a secondary alcohol group CHOH (see p. 568). Nitric acid oxidises lactic acid to oxalic acid. Chromic acid converts it into acetic acid, CO_2 and H_2O. Since lactic acid is hydroxypropionic, it may be reduced to propionic acid by strong hydriodic acid; $C_2H_4(OH){\cdot}CO_2H + 2HI = C_2H_5{\cdot}CO_2H + H_2O + I_2$. Conversely, propionic acid may be converted into lactic by the following steps: (1) $CH_3{\cdot}CH_2{\cdot}CO_2H + Br_2 = CH_3{\cdot}CHBr{\cdot}CO_2H + HBr.$; (2) $CH_3{\cdot}CHBr{\cdot}CO_2H + KOH = CH_3{\cdot}CHOH{\cdot}CO_2H + KBr$.

Lactic acid is producible from aldehyde through its HCN derivative (see above).

The *lactates* are mostly soluble; the most important of them is the *zinc lactate* $(C_2H_5O{\cdot}CO_2)_2Zn.3H_2O$, which is sparingly soluble in water, and is precipitated in prismatic crystals when zinc sulphate is added to lactic acid neutralised by ammonia. Salts of the type $CH_3{\cdot}CHOM{\cdot}CO_2M$ are known: thus *sodium sodio-lactate*, $CH_3{\cdot}CHONa{\cdot}CO_2Na$, is prepared by the action of sodium on sodium lactate.

378. Stereoisomerism as Illustrated by Ethylidene Lactic Acid.—Ethylidene lactic acid is also found in juice of flesh (Liebig's extract of meat), in bile, and in the urine of persons poisoned by phosphorus. This lactic acid has been termed *sarcolactic acid* or *paralactic acid*, because it is not identical in all its properties with the fermentation lactic acid described above. Chemically speaking, the difference is exceedingly slight, amounting mainly to a greater solubility of zinc sarcolactate (which crystallises with $2H_2O$) than of zinc fermentation lactate, and a smaller solubility of the calcium salt ($4H_2O$). The physical difference between the two is considerable, for whilst the fermentation acid is inactive towards polarised light, sarcolactic acid rotates the plane of polarisation to the right. This property leads to the distinctive titles, *dextro-ethylidene lactic acid* for sarcolactic acid, and *inactive ethylidene lactic acid* for the fermentation acid. If kept in a desiccator for some time, the dextro-acid becomes converted into an anhydride the solution of which is lævo-rotatory, but the lactide obtained by heating the acid yields inactive lactic acid when dissolved. The salts of the dextro-acid are lævo-rotatory.

When cane sugar is fermented by means of a certain bacillus, a *lævo-ethylidene lactic acid* is produced, the salts of which are dextro-rotatory.

It seems that there are three ethylidene lactic acids, which may be distinguished as *i*-, *d*-, and *l*- ethylidene lactic acid respectively. But when equal weights of the *d*- and *l*- acids are mixed together the product is found to be optically inactive; hence it may be concluded that the inactive acid is made up of an equal number of molecules of the

d- and *l*- acids, which neutralise each other, so that in considering a theory to account for the existence of these three acids, it is only necessary to attempt to explain the isomerism of the dextro- and lævo-modifications. The theory of position isomerism, already mentioned, will not suffice to furnish an explanation, because the only possible position isomeride of ethylidene lactic acid, according to the theory, is ethylene lactic acid, from which both the *d*- and the *l*- acids differ chemically.

The examination of a large number of compounds which are optically active has shown that each contains one or more carbon atoms to which are attached four different elements or radicles; thus, in ethylidene lactic acid, $CH_3{\cdot}CHOH{\cdot}COOH$, the middle carbon atom has each of its atom-fixing powers satisfied by a different radicle; viz., CH_3, H, OH, and COOH. Such a carbon atom is said to be *asymmetric*, and it is believed that *an optically active compound is one which possesses one or more asymmetric carbon atoms.**

Several cases of isomerides differing from each other in optical activity have been noticed in the preceding pages; in each case it will be found that the accepted formula for the compound contains one or more asymmetric carbon atoms. Thus three of the 14 isomeric amyl-alcohols (p. 569) occur in the *d*-, *l*-, and *i*-form; and in each the original methane carbon atom has four different radicles attached to it, namely in one—CH_3, $CH_3{\cdot}CH_2$, H and CH_2OH; in another—CH_3, $CH_3{\cdot}CH_2{\cdot}CH_2$, H and OH; and in the third—CH_3, $(CH_3)_2CH$, H and OH.

Where a compound contains more than one asymmetric carbon atom the cases of isomerism are more numerous and such will receive notice under *Tartaric Acid* and the *Sugars*.

No hypothesis has been suggested upon which it is possible to prophesy whether a given compound, containing an asymmetric carbon atom will be dextro- or lævo-rotatory.

The most fruitful hypothesis for explaining the existence of *d*- and *l*-isomerides having an asymmetric carbon atom is that the four groups attached to this carbon atom are differently arranged in space, in the two isomerides, which are therefore called *stereoisomerides* (στερεός, *solid*). If the carbon atom be considered to occupy the centre of a tetrahedron in space, as suggested at p. 534, it will be found that no essentially different structures can be made, unless each corner of the tetrahedron has a different radicle attached to it.

For if two tetrahedra be constructed, the corners of which are represented by A, A, A, B, or A, A, B, B, or A, A, B, C, or any combination of four letters, two or more of which are the same, it will be found to be always possible to put the one tetrahedron inside the other in such a manner that the four letters on the corners of the one shall coincide with the four letters on the corners of the other. If, however, the four corners of each be represented by the four different letters A, B, C, D, it will be found possible so to arrange these letters that the one tetrahedron cannot be introduced into the other in such a manner that the four corners correspond. The arrangement necessary will be understood from the statement that if the observer be opposite those faces of the tetrahedra which are similarly lettered the order of the letters on the one face will be the reverse of the order of the letters on the other face: if the letters A, B, C, for instance, be in the order of the motion of the hands of a clock on the face of one tetrahedron they will be in the reverse order, C, B, A, on the face of the other. Such an arrangement is depicted in Fig. 274, from

* *Cf.* Amyl alcohol (p. 569).

which it will be seen that the two arrangements bear the same relationship to each other as an object bears to its image.

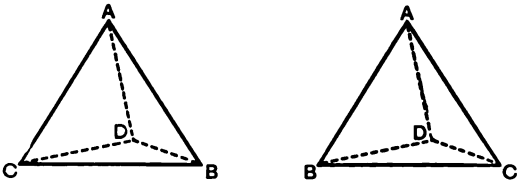


Fig. 274.

It is in the above manner that Le Bel and Van't Hoff have sought to explain why no isomerides of methane substitution-products, except of those of the type $CR_1R_2R_3R_4$, exist. If the compound which is arranged in the clock-wise manner in Fig. 274 be dextro-rotatory, then that which is anticlock-wise will be lævo-rotatory.

The theory has been tested by investigating compounds which, by the process of their formation, ought to contain an asymmetric carbon atom, although they were known only in an inactive form. By appropriate treatment many such compounds have been resolved into a dextro- and lævo-form; the principal methods of treatment are—(1) Crystallisation from water, advantage being taken of the greater solubility of one of the active forms; in this manner the zinc-ammonium salt of *i*-lactic acid has been resolved into the zinc-ammonium salts of the *d*- and *l*-acids. (2) Treatment of the inactive compound with another active compound, and crystallising the product; thus, if the inactive compound is acid it is crystallised with an active base, such as strychnine; if it is basic it is crystallised with an active acid, such as tartaric acid. In either case, the salt formed is separated by crystallisation into a *d*- and *l*- modification, the one or the other being the more soluble. Fermentation lactic acid is split up by crystallising it with strychnine, the *l*-strychnine lactate separating first. (3) Fermentation of the inactive compound with some bacillus which feeds on one of the active forms rather than upon the other; some fungi show a similar preference.

The second method has proved the most fruitful, and by its means optically active sulphur, tin and nitrogen compounds, containing an asymmetric S, Sn, and N atom respectively, have been prepared.

As Sn falls in the same periodic group as C (p. 302) and is a true tetravalent element, the fact that it forms optically active compounds is of particular interest. By a series of reactions, which will be understood better after the student has perused the section on *organo-mineral* compounds, an inactive *methylethylpropyl tin iodide*, $\begin{matrix}CH_3\\C_2H_5\end{matrix}\!\!>\!Sn\!<\!\begin{matrix}C_3H_7\\I\end{matrix}$, has been obtained. This obviously contains an asymmetric tin atom, and by treating it with the silver salt of an optically active acid, *d-camphorsulphonic acid*, so as to exchange the iodine for the radicle of the active acid, and then evaporating the solution, crystals are obtained which are more dextro-rotatory than is the *d*-camphorsulphonic acid. From these crystals a dextro-rotatory methylethylpropyl tin iodide is obtained by treatment with KI.

Sulphur is in the sixth group of the periodic classification; nevertheless, there are some organic derivatives of this element in which it appears to be tetravalent, *e.g.*, the *thetines*. One of these is prepared by the action of *bromacetic acid*, $CH_2Br{\cdot}COOH$, on *methylethylsulphide*, $CH_3{\cdot}S{\cdot}C_2H_5$; it is inactive, and is known as *methylethylthetine bromide*, $\begin{matrix}Br\\C_2H_5\end{matrix}\!\!>\!S\!<\!\begin{matrix}CH_3\\CH_2{\cdot}COOH\end{matrix}$. If this view of the structure of the thetine is correct, the S atom is asymmetric and the inactive compound should be capable of yielding optically active components. By applying *d*-camphorsulphonic acid in the manner described above, the *d*-form has been isolated.

The discovery of optically active nitrogen compounds has extended the theory of the connection between asymmetry and optical activity to pentavalent elements.

If, in ammonium iodide, NH_4I, there is substituted for each H atom a different hydrocarbon radicle, an asymmetric nitrogen compound will be produced. Such quaternary ammonium compounds are well known, and lately one, *benzylphenylallylmethylammonium iodide*, $N(C_6H_5{\cdot}CH_2)(C_6H_5)(C_3H_5)(CH_3)I$, has been resolved into optically active components by the aid of *d*-camphorsulphonic acid.

Ethylene lactic acid, or *β-hydroxypropionic acid*, $CH_2(OH){\cdot}CH_2{\cdot}CO_2H$, is also found in juice of flesh, and is made by treating β-iodopropionic acid, $CH_2I{\cdot}CH_2{\cdot}CO_2H$, with moist silver oxide. Its formula is confirmed by its formation from glycol chlorhydrin, $CH_2Cl{\cdot}CH_2OH$ (and therefore from ethylene, p. 575), by conversion into the cyanohydrin, $CH_2CN.CH_2OH$, and hydrolysis of the latter. It is a syrupy mass, and is distinguished from ethylidene lactic acid by yielding no anhydrides, but acrylic acid, $CH_2:CH{\cdot}CO_2H$, and water, when heated; hence it is sometimes called *hydracrylic acid*. This is characteristic of β-alcohol acids, which generally yield αβ-olefine acids when heated.

When oxidised it yields carbonic and oxalic acids instead of acetic. Its zinc salt ($4H_2O$) is very soluble in water.

379. *Hydroxybutyric acids* are four in number: the α-acid, $CH_3{\cdot}CH_2{\cdot}CH(OH){\cdot}CO_2H$, the β-acid, $CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CO_2H$, the γ-acid, $CH_2OH{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$, and the α-iso-acid $(CH_3)_2{:}C(OH){\cdot}CO_2H$. A fifth, viz., the β-iso-acid $(CH_3)(CH_2OH){:}CH{\cdot}CO_2H$ is obviously possible, but is not known.

The γ-hydroxy-acids are very unstable, and when an attempt is made to liberate them from their salts by addition of a more powerful acid they immediately lose water, becoming "intramolecular anhydrides," or *lactones*. These are interesting compounds, for they may be regarded as internally formed ethereal salts (*cyclic esters*), just as ethyl acetate is an externally formed ethereal salt (*cf.* glycol-glycollic acid, p. 604). Thus, γ-hydroxybutyric acid, $\begin{matrix}CH_2{\cdot}CH_2OH\\ \vdots\\ CH_2{\cdot}COOH\end{matrix}$, yields *butyrolactone*, $\begin{matrix}CH_2{\cdot}CH_2\\ \vdots\\ CH_2{\cdot}CO\end{matrix}\!\!>\!O$. The acids containing five carbon atoms can yield δ-hydroxy acids and these lose water forming *δ-lactones*. Both γ- and δ-lactones are fairly stable, being only partially converted into the corresponding acids by boiling water, but into salts of these acids by alkalies.

α-Hydroxycaproic acid, or *leucic acid*; *see* Leucine.

Ricinoleic and *iso-ricinoleic acids* are *hydroxyoleic acids*, $C_{17}H_{33}(OH){\cdot}CO_2H$, which occur as glycerides in castor oil.

379*a*. **Polyhydroxy-monobasic acids.**—*Glyceric acid*, $CH_2OH{\cdot}CHOH{\cdot}CO_2H$, is a primary-secondary-alcohol-acid; it has been already mentioned as an oxidation product of glycerine. When produced in this way it is optically inactive, but both an *l*- and a *d*- variety have been obtained.

A number of polyhydric monobasic acids is produced by the oxidation of the sugars; these are known as *hexonic acids*, $CH_2OH{\cdot}[CHOH]_4{\cdot}CO_2H$. They are stereoisomerides of each other, being either *d*- acids, *l*- acids, or *i*- acids. They will receive further notice under the sugars.

379*b*. **Aldehyde-acids.**—*Glyoxylic*, or *glyoxalic acid*, $CHO{\cdot}CO_2H$, is a product of the oxidation of glycol and of alcohol. It crystallises in prisms and distils with steam. Being aldehydic in nature, it forms a crystalline compound with $NaHSO_3$ and reduces silver salts, being thereby oxidised to oxalic acid.

Glycuronic acid, $CHO{\cdot}[CHOH]_4{\cdot}CO_2H$, is obtained by reducing saccharic acid (*q. v.*) with sodium amalgam; it is a syrup which is readily converted into a lactone (see above).

380. **Monobasic Acids from Hydroxy-Benzenes.**—The OH groups in these acids may be attached either to the benzene nucleus, in which case the acids are *phenol acids*, not alcohol-acids, or they may occur in the side-chain, in which case the acid is an alcohol-acid; thus, *salicylic acid* is a phenol-acid, $C_6H_4(OH){\cdot}COOH$, whilst *phenyl-glycollic acid* is an alcohol-acid, $C_6H_5{\cdot}CHOH{\cdot}COOH$.

The most important *general reactions for obtaining the phenolic acids* are as follows: (1) The sodium phenols are heated with CO_2 (see salicylic acid). (2) The phenols are boiled with CCl_4 and KOH; $C_6H_5OH + CCl_4 + 5KOH = C_6H_4(OH)\cdot COOK + 4KCl + 3HOH$. (*Cf.* the method for making hydroxy-aldehydes; p. 585.) (3) The homologues of phenol are oxidised by fusion with KOH; $C_6H_4(OH)\cdot CH_3 + 2KOH = C_6H_4(OK)\cdot COOK + 3H_2$.

The alcohol-acids are made by reactions similar to those used in making the paraffin alcohol-acids.

Like the alcohol-acids, the phenol-acids yield two classes of salts, *e.g.*, $C_6H_4(OH)\cdot CO_2Na$, and $C_6H_4(ONa)\cdot CO_2Na$, the former being produced when the acid is dissolved in Na_2CO_3, the latter when NaOH is used.

Hydroxybenzoic acids, $C_6H_4(OH)\cdot CO_2H$.—Being di-substituted benzenes, these are three in number. The most important is the 1 : 2-acid or **salicylic acid.** This is prepared artificially by combining phenol with soda, and heating the product in carbonic acid gas.

The phenol, with half its weight of NaOH, is dissolved in a little water and evaporated to dryness. This sodium-phenol is powdered, placed in a flask or retort, and heated at 100° C. in a slow stream of dry CO_2 for some hours. The temperature is then raised to 180° C., when phenol distils over, and continues to do so till the temperature has risen to 250° C. The residue is dissolved in a small quantity of water, and strong HCl added to precipitate the salicylic acid, which may be purified by crystallisation from water.

By dissolving phenol in soda, sodium-phenol is produced—

$$C_6H_5\cdot OH + NaOH = C_6H_5\cdot ONa + HOH.$$

When this is heated in CO_2, it yields phenol and sodio-salicylate of sodium; $2C_6H_5ONa + CO_2 = C_6H_5OH + C_6H_4(ONa)\cdot CO_2Na$; this last, decomposed by HCl, yields salicylic acid—

$$C_6H_4(ONa)\cdot CO_2Na + 2HCl = C_6H_4(OH)\cdot CO_2H + 2NaCl.$$

Salicylic acid was formerly made from *oil of winter-green* (*Gaultheria*, a North American plant of the heath order), which is the *methyl salicylate*, $C_6H_4(OH)\cdot CO_2CH_3$. Its original source was salicin, a glucoside extracted from willow-bark, which yields the salicylate when fused with potash. Salicylic acid has been found in the leaves, stems, and rhizomes of some of the *Violaceæ*, and in the garden-pansy.

Properties of salicylic acid.—It forms four-sided prisms which fuse at 155° C., and sublime, if carefully heated; but a temperature of 220 decomposes it into phenol and CO_2; $C_6H_4(OH)\cdot CO_2H = CO_2 + C_6H_5\cdot OH$. This change occurs more readily in presence of an alkali, to absorb the CO_2. It dissolves sparingly in cold water, more easily on heating, and is soluble in alcohol and ether. Its solution gives an intense violet colour with ferric chloride, a reaction not exhibited by the *p*- and *m*-hydroxybenzoic acids. It possesses antiseptic properties, and is used for the preservation of articles of food, being free from taste and smell. It is also used in making dyes, and *sodium salicylate* is a well-known anti-rheumatic.

The salicylates of K and Na are crystalline: barium salicylate $(C_6H_4OH\,CO_2)_2Ba.Aq$, also crystallises, and, when boiled with baryta-water, yields a sparingly soluble salt, $C_6H_4BaOCO_2.2Aq$, in which the diad Ba is exchanged for the H of the hydroxyl as well as that of the carboxyl.

Anisic acid, or *para-methoxybenzoic acid*, $C_6H_4(OCH_3)\cdot CO_2H$, is isomeric with oil of winter-green, and is formed by the oxidation of its aldehyde, which occurs in oil

of anise (p. 586). It may be formed artificially from salicylic acid by heating its potassium salt to 220° C., when it yields di-potassium parahydroxy-benzoate, which is converted into potassium anisate when treated successively with methyl iodide and caustic potash—

$$2(C_6H_4(OH)\cdot CO_2K) = C_6H_5\cdot OH + CO_2 + C_6H_4(OK)\cdot CO_2K.$$

$C_6H_4(OK)\cdot CO_2K + 2CH_3I = C_6H_4(OCH_3)\cdot CO_2CH_3$ (*methyl anisate*) + 2KI; $C_6H_4(OCH_3)\cdot CO_2CH_3 + KOH = C_6H_4(OCH_3)\cdot CO_2K$ (*potassium anisate*) + $CH_3\cdot OH$. Hydrochloric acid precipitates the anisic acid, which may be dissolved in alcohol and crystallised. It forms prisms fusing at 185° C. and subliming undecomposed.

Hydroxytoluic acids or *cresotinic acids* $C_6H_3(CH_3)(OH)\cdot COOH$ are ten in number as they are trisubstitution products with 3 different radicles. All the possible isomerides are known.

Protocatechuic or **dihydroxybenzoic acid**, $C_6H_3(OH)_2\cdot CO_2H$ [$CO_2H : (OH_2) = 1 : 3 : 4$], is prepared by the action of fused caustic soda on the large class of bodies known as *gum-resins*, and acquired its name from its production in this way from *catechu* (*Cutch* or *Terra japonica*), a substance much used in dyeing black, extracted by boiling water from the inner bark wood of the *Mimosa catechu* of the East Indies; *kino*, a gum-resin exuding from certain Indian and African leguminous plants, and employed in medicine as an astringent, also yields the acid. It crystallises in plates or needles containing H_2O, which fuse at 199° C., and are soluble in water, alcohol, and ether. Ferric chloride gives a green colour with the acid, which is changed to blue and red by alkalies. When heated, it is decomposed, yielding *pyrocatechol*; $C_6H_3(OH)_2\cdot CO_2H = CO_2 + C_6H_4(OH)_2$.

It will be found that the formation of this acid during the *potash-fusion* of an organic substance often throws light upon its constitution.

Vanillic or *3-methyl-protocatechuic acid*, $C_6H_3(OH)(OCH_3)\cdot CO_2H$, is produced when vanillic aldehyde (vanillin) is exposed to moist air. It may also be made by oxidising the glucoside coniferin with potassium permanganate. It crystallises in plates, fusing at 211° C. and subliming unchanged. When heated in a sealed tube with dilute HCl at 160° C., it yields protocatechuic acid and methyl chloride; $C_6H_3(OH)(OCH_3)\cdot CO_2H + HCl = C_6H_3(OH)_2\cdot CO_2H + CH_3Cl$.

381. **Aromatic Paraffin Alcohol-acids.**—*Mandelic acid* or *phenylglycollic acid*, $C_6H_5\cdot CH(OH)\cdot CO_2H$, is prepared from amygdaline (*q.v.*) or by the hydrolysis of the hydrocyanic compound of benzaldehyde, $C_6H_5\,CH(OH)CN$. It melts at 133° C. and is soluble in water. It exists in stereoisomeric forms, which is to be expected from the presence of an asymmetric carbon atom.

382. *Trihydroxybenzoic acids.*—Of the six possible isomerides gallic acid is the most important.

Gallic acid, $3:4:5-C_6H_3(OH)_3\cdot CO_2H$ * is produced by the hydrolysis of the tannin in gall-nuts (gallotannic acid), $C_{14}H_{10}O_9\cdot CO_2 + H_2O = 2C_6H_2(OH)_3\cdot CO_2H$. It is therefore prepared either by boiling the tannin with dilute sulphuric acid, or by keeping the moistened powdered nut-galls some weeks in a warm place, so that they may undergo fermentation, and extracting the gallic acid with boiling water, from which it crystallises in fine needles containing H_2O. It dissolves in 3 parts of boiling water and 100 of cold water. It becomes anhydrous at 100° C., and melts at about 220° C., yielding a crystalline sublimate of pyrogallol; $C_6H_2(OH)_3\cdot CO_2H = C_6H_3(OH)_3 + CO_2$.

Solution of gallic acid is not precipitated by H_2SO_4 or HCl, or by gelatine. Lead acetate precipitates it, but the precipitate is soluble in acetic acid. Alum and potash give a precipitate easily soluble in potash. Copper sulphate does not precipitate it immediately. Ferric salts give a bluish-black precipitate, and the alkalies give a brown-red colour, especially on exposure to air. Alcoholic alkali converts gallic acid into a yellow dye-stuff, *galloflavin*, $C_{13}H_6O_9$. Gallic acid is found in several vegetable products, some of which are used in dyeing and tanning; as in *divi-divi*, the fruit of a leguminous plant (*Cæsalpinia coriaria*), in sumach, in

* In expressing orientation it is customary to assume that the characteristic group of a compound occupies position 1, and to name the positions of the other groups relatively to this. Thus 3:4:5-trihydroxybenzoic acid means that if the CO_2H group has position 1, the OH groups will be 3:4:5.

mangoes, and the leaves of the wild vine, a tropical plant of the Moon-seed order (*Cissampelos pareira*), useful in medicine.

Gallic acid may be obtained artificially by heating di-iodosalicylic acid with solution of potassium carbonate to 140° C. in a sealed tube—

$$C_6H_2I_2(OH)\cdot CO_2H + K_2CO_3 + H_2O = C_6H_2(OH)_3\cdot CO_2H + 2KI + CO_2.$$

When gallic acid is heated with 4 parts of strong H_2SO_4 to 75° C., it gives a dark-red solution; and if this be cooled and poured into water, a red precipitate is obtained which has the composition $C_{14}H_8O_8.2Aq$, or twice gallic acid, minus $2H_2O$. This was formerly termed *rufigallic acid*, but is really *hexa-hydroxy-anthraquinone*, $C_{14}H_2(OH)_6O_2$, for zinc-dust reduces it to anthracene, $C_{14}H_{10}$.

Ellagic acid, $C_{13}H_5O_6\cdot CO_2H$, is obtained by oxidising gallic acid with arsenic anhydride; it is a yellowish crystalline powder sparingly soluble in water and alcohol. It is found in *bezoar-stones*, the calculi sometimes formed in the intestines of wild goats in Persia.

Basic bismuth gallate, $C_6H_2(OH)_3\cdot COOBi(OH)_2$ is an antiseptic sold as *dermatol*.

383. **Tannic acid** or *tannin*.—This name has been applied to a number of plant-constituents, all of which are capable of precipitating gelatine, and therefore of more or less completely tanning hide into leather. They are also characterised by the dark blue or green colour which they give with ferrous salts; hence their use in the manufacture of inks. The tannins apparently occur in the plants as unstable glucosides, and when hydrolysed they are converted into glucoses and monobasic acids which seem to be related to the polyhydroxybenzoic acids. The only tannic acid which can be said to be thoroughly known is that obtained from gall-nuts, and commonly called *gallotannic acid*, $C_{13}H_9O_7\cdot CO_2H + 2H_2O$.

240 grammes of powdered gall-nuts are digested for some hours, with frequent shaking, with 1800 cubic centimetres of ether and 150 of water. The mixture is poured into a funnel loosely plugged with cotton, and the filtered liquid allowed to stand, when it separates into two layers, the upper one being the ethereal solution of colouring-matter, &c., and the lower an aqueous solution of tannic acid, which is evaporated to dryness at a low temperature.

Gallotannic acid does not crystallise, but is left, on evaporation, in brownish-white shining scales, which are very easily soluble in water, but sparingly in alcohol and in anhydrous ether. Its solution is astringent, feebly acid, and gives a bluish-black precipitate with ferric chloride. H_2SO_4 and HCl combine with it to form white precipitates, and a solution of gelatine precipitates a very insoluble compound with tannic acid. By hydrolysis gallotannic acid yields gallic acid (p. 609).

The view that gallotannic acid is identical with *di-gallic acid*—

$$C_6H_2(OH)_3\cdot CO\cdot O\cdot C_6H_2(OH)_2\cdot COOH,$$

which represents two molecules of gallic acid *minus* one molecule of water, and is produced by action of dehydrating agents (*e.g.*, $POCl_3$ at 130° C.) on gallic acid, has been proved incorrect.

Albumin, starch, and most of the alkaloids are also precipitated by tannic acid. Common salt causes the separation of tannic acid from its solution. Lead acetate precipitates it as basic tannate, which is insoluble in acetic acid. Copper sulphate also precipitates it immediately. Alum and potash added to tannic acid give a precipitate insoluble in cold potash. Potash or ammonia added to a solution of tannic acid renders it brown, especially if shaken with air, absorption of oxygen occurring. Tannic acid acts as a reducing-agent upon alkaline cupric solutions, producing cuprous oxide. It is decomposed by distillation, one of the products being *pyrogallol*, $C_6H_3(OH)_3$.

Alcoholic solutions of tannic acid and potash yield a precipitate of *potassium tannate*, $C_{13}H_9O_7\cdot CO_2K$, and if this is dissolved in water, and $BaCl_2$ added, *barium tannate*, $(C_{13}H_9O_7\cdot CO_2)_2Ba$, is precipitated.

The tannic acids or tannins used in commerce, in the form of extracts of various parts of plants, are slightly different in properties, and pending exact knowledge as to their constitution, they are distinguished by names implying the

sources from which they are derived. Thus, *querci-tannic acid* is from oak-bark, *quino-tannic acid* from cinchona bark, *caffeo-tannic acid* from coffee, *moritannic acid* from fustic (a yellow dyewood from a tree of the Mulberry order, *Morus tinctoria*).

Sumach, the leaves of the *Rhus coriaria*, a tropical plant of the Cashew order, and *Myrobalans*, the fruit of several species of *Terminalia*, Indian trees, contain gallotannic acid. Myrobalans also contains *ellagitannic acid*, very similar to gallotannic acid, and likewise contained in *diri-diri*.

The tannins may be classified into *pyrogallol-tannins* and *pyrocatechol tannins*, accordingly as they yield pyrogallol or pyrocatechol when heated. Those belonging to the first class yield gallic and ellagic acids when heated with alkalies, whilst those of the latter class yield protocatechuic acid, and either phlorogiucol or acetic acid, by the same treatment. The deposit of ellagic acid which is formed by the oxidation of pyrogallol tannins is probably the "bloom" noticed by tanners on the surface of leather prepared by means of materials such as myrobalans, sumach, and divi-divi. The pyrocatechol tannins are liable to deposit complex anhydrides termed phlobaphenes,* which have a red colour; such are the tannins of oak bark, *mimosa* and *ralonia*.

Quinic or *kinic acid*, or *hexahydrotetrahydroxybenzoic acid*, $C_6H_7(OH)_4{\cdot}CO_2H$, is a hydroxy-acid from hexahydrobenzene (p. 550) found in cinchona bark, in coffee and some other plants. It is crystalline, soluble, and melts at 162° C. It gives pyrocatechol when distilled, and protocatechuic acid when fused with KOH. When heated with MnO_2 and H_2SO_4, it is oxidised to quinone, which sublimes in yellow needles.

383*a*. **Hydroxyphenyl-Fatty and Olefine Acids.**—These may be regarded as phenols in which a nucleal H atom has been exchanged for an open-chain acid radicle. There are three position isomerides of each of the monohydroxyacids.

1 : 2-*Hydroxyphenylacetic acid*, $C_6H_4(OH){\cdot}CH_2{\cdot}COOH$, melts at 137° C. and is important as a relative of indigo.

1 : 2-*Hydroxy-β-phenylacrylic acid* or 1 : 2-*hydroxycinnamic acid*—

$$C_6H_4(OH){\cdot}CH : CH{\cdot}COOH$$

commonly called *coumaric acid* is obtained from 1 : 2-*amidocinnamic acid*—

$$C_6H_4(NH_2){\cdot}CH : CH{\cdot}COOH$$

through the diazo-reaction; it melts at 208° C. Its salts are also obtained from coumarin by heating it with alkalies. *Coumarin* is the lactone of coumaric acid, $C_6H_4\begin{cases}O\ -\ CO\\ \quad\quad\ |\\ CH\ :\ CH\end{cases}$, and is the substance which causes the smell of hay and of the Tonka bean (*Coumaroma odorata*) from which it may be extracted by boiling with alcohol, when crystals of coumarin are deposited on cooling. It is made artificially by heating salicyl aldehyde with sodium acetate and acetic anhydride (*cf.* cinnamic acid, p. 601). The salts from coumarin are however isomeric with those prepared from coumaric acid, the origin of the isomerism being still unknown.

Caffeic acid, or *dihydroxy-cinnamic acid*, $[(OH)_2 : (CH : CH{\cdot}CO_2H) = 3 : 4 : 1]$, is obtained by boiling with KOH the residue left on evaporating the aqueous decoction of coffee, and precipitating the solution by HCl. It crystallises in plates (m.-p. 213° C.) on cooling, and is soluble in alcohol. It yields pyrocatechol when heated, and is converted into acetate and protocatechuate when fused with KOH.

Piperic Acid is derived from a 3 : 4-dihydroxyphenyldiolefine acid, *dihydroxy-cinnamenylacrylic acid*, by substituting methylene, CH_2, for the two H atoms of the two OH groups; hence its formula is 3 : 4-$CH_2\begin{cases}O\\ O\end{cases}C_6H_3{\cdot}CH : CH{\cdot}CH : CH{\cdot}COOH$.

It melts at 217° C. and is found as a derivative of piperidine (*q.v.*) in pepper.

384. **Dibasic Acids from Paraffin Hydrocarbons (Oxalic or Succinic Series), $C_nH_{2n}(COOH)_2$.**—These acids may be regarded as derived from the hydrocarbons by substitution of two COOH groups for two H atoms. They are oxidation products of diprimary glycols, as might be expected (p. 574), and are also obtainable by nucleal condensa-

* φλοιός, *bark*; βαφή, *colour*.

tion from the fatty acids, as for instance when bromacetic acid is treated with metallic silver, producing succinic acid :—

$$HOOC{\cdot}CH_2Br + BrCH_2{\cdot}COOH + Ag_2 = HOOC{\cdot}CH_2{\cdot}CH_2{\cdot}COOH + 2AgBr.$$

These methods are not much used, however; more important is the introduction of the CN group into a fatty acid and hydrolysis of the product. Thus, hydrolysis of cyanoacetic acid, obtained from chloracetic acid by action of KCN, yields malonic acid :—

$$CH_2Cl{\cdot}COOH \rightarrow CH_2CN{\cdot}COOH \rightarrow CH_2(COOH)_2 \text{ (}cf.\text{ p. 587).}$$

An analogous method is the hydrolysis of the dicyanides of the olefine radicles, $CH_2CN{\cdot}CH_2CN$ yielding succinic acid, for example.

Isomerism among these acids is like that among other disubstituted paraffins (p. 567).

The typical members of the series are malonic acid, $CH_2\begin{matrix}COOH\\COOH\end{matrix}$, and succinic acid, $\begin{matrix}CH_2COOH\\CH_2COOH\end{matrix}$. Acids like the former, in which the two carboxyls are attached to the same carbon atom break up when heated with formation of CO_2 and an acid of the acetic series. Acids of the succinic type, in which the carboxyls are attached to different carbon atoms, lose water and yield internal anhydrides, like $\begin{matrix}CH_2{\cdot}CO\\CH_2{\cdot}CO\end{matrix}\!\!>\!O$, when heated; this behaviour, however, is not shown by acids in which the COOH groups are separated by more than three CH_2 groups. Both types lose CO_2 when fused with KOH, yielding an acid of the acetic series.

385. **Oxalic acid,** $(CO_2H)_2$, is the final product of the oxidation of glycol, and one of the products of the hydrolysis of cyanogen, $CN{\cdot}CN + 4HOH = COOH{\cdot}COOH + 2NH_3$. It is prepared on the small scale by oxidising sugar with nitric acid, and on the large scale by oxidising sawdust with potash.

Preparation of oxalic acid from sugar.—50 grms. of sugar are gently heated in a flask with 250 c.c. of ordinary concentrated nitric acid, sp. gr. 1.4. After the action commences, remove the heat, when the oxidation will continue violently. On cooling, part of the oxalic acid crystallises, and more is obtained by concentrating the mother-liquor. Drain the crystals on a funnel, and dissolve them in as little boiling water as possible, so as to purify the acid by re-crystallisation. It may be allowed to dry by exposure to air.

Preparation of oxalic acid from sawdust.—Common pine sawdust is made into a thick paste with a solution containing $KOH + 2NaOH$ of sp. gr. 1.35. This is spread on iron plates, dried up, and heated just short of carbonisation. The cellulose, $C_6H_{10}O_5$, is thus oxidised, with evolution of hydrogen, and converted into oxalic acid, which remains in the mass as oxalates of potassium and sodium. These are dissolved in water, and boiled with lime, which produces the insoluble calcium oxalate, together with solution of the caustic alkalies, which may be used again. The calcium oxalate is decomposed by dilute sulphuric acid, the solution of oxalic acid filtered from the calcium sulphate and crystallised.

Strictly speaking, in carrying out this process, the fused mass is treated with a small quantity of hot water, which leaves the bulk of the sodium oxalate undissolved: this is decomposed by lime, as stated above. The liquor, which contains but little oxalate, is boiled to dryness, the residue heated, and the alkaline carbonate causticised by lime. It is worth noting that caustic soda alone would produce very little oxalate. When potash is cheap, it may be used alone.

Oxalic acid occurs in sorrel, rhubarb, and many other plants. Potassium oxalate is formed when potassium formate is gently heated; $2(H{\cdot}CO{\cdot}OK) = H_2 + (CO_2K)_2$. Sodium oxalate is produced when sodium, mixed with sand to moderate the action, is heated at 360° C. in dry CO_2; $Na_2 + 2CO_2 = (CO_2Na)_2$.

Properties of oxalic acid.—It forms monoclinic prisms containing 2Aq, which are soluble in nine parts of cold water and in alcohol. It is a very strong acid, able to decompose the nitrates and chlorides. In large doses it is poisonous. When gently heated, the crystals effloresce, from loss of water, and begin to vaporise slowly at 100° C. When sharply heated the crystallised acid melts at 101° C. and the anhydrous at 189° C. At 165° it sublimes freely, part being decomposed into formic acid and CO_2; $(CO_2H)_2 = H{\cdot}CO_2H + CO_2$. A weak solution of oxalic acid is decomposed by boiling. When heated with strong sulphuric acid, $(CO_2H)_2 = CO_2 + CO + H_2O$, the CO burning on applying a flame. From twelve parts of warm oil of vitriol the acid crystallises in large rhombic octahedra, which are anhydrous. Oxalic acid is largely used in dyeing, calico-printing, and bleaching, in cleaning brass, and in removing iron-mould from linen.

Normal potassium oxalate, $(CO_2K)_2.Aq$, is moderately soluble in water. *Hydropotassium oxalate*, or *potassium binoxalate*, or *salt of sorrel*, is $(CO_2)_2KH$. It is also called *essential salt of lemons*, though lemons contain no oxalic acid. It dissolves in 40 parts of cold water, and has occasionally caused accidents by being mistaken for cream of tartar, potassium hydrogen tartrate, from which it is readily distinguished by the action of heat, which chars the tartrate, but not the oxalate.

Trihydropotassium oxalate, or *potassium quadroxalate*, $(CO_2)_2H_3K.2Aq$, is more commonly sold as salt of sorrel, and sometimes as salt of lemon. It is even less soluble than the preceding.

Sodium oxalate, $(CO_2Na)_2$, is found in various plants which grow in salt marshes. It is less soluble than potassium oxalate. The alkali oxalates, when heated, evolve CO and leave carbonates, $(CO_2K)_2 = CO + CO(OK)_2$.

Ammonium oxalate, $(CO_2NH_4)_2.Aq$, occurs in Peruvian guano. It is used in analysis for the precipitation of calcium, and crystallises, in needles, from solution of oxalic acid neutralised with ammonia.

Calcium oxalate, $(CO_2)_2Ca.Aq$, is often found crystallised in plant-cells. Some lichens growing on limestones contain half their weight of calcium oxalate. It is occasionally found in urine and in calculi. Calcium chloride is the best test for oxalic acid, giving a white precipitate insoluble in acetic acid. When heated, $(CO_2)_2Ca = CO + CaCO_3$.

Ferrous oxalate, $(CO_2)_2Fe$, occurs as *oxalite* in brown coal. *Ferric oxalate*, $(CO_2)_6Fe_2$, when exposed to sunlight in presence of water, evolves CO_2, and deposits a yellow crystalline precipitate of $(CO_2)_2Fe.2Aq$. Ferric oxalate is used in photography. *Potassium ferrous oxalate*, $(CO_2)_4K_2Fe$, prepared by adding potassium oxalate in excess to ferrous sulphate, is a very powerful reducing-agent, used as a photographic developer.

Potassium chromic oxalate, $(CO_2)_6K_3Cr.3Aq$, is obtained in crystals so intensely blue as to look black, by dissolving in hot water 1 part of potassium dichromate, 2 parts of hydropotassium oxalate, and 2 parts of oxalic acid. Neither the oxalic acid nor the Cr_2O_3 can be precipitated from this salt by the usual tests.

Potassium calcium chromic oxalate, $(CO_2)_6KCaCr.3Aq$, is soluble in water, and gives a precipitate of calcium oxalate on adding calcium chloride.

Barium chromic oxalate, $(CO_2)_{12}Ba_3Cr_2.8Aq$, is also a soluble salt, and, when decomposed by sulphuric acid, yields a red solution which probably contains the acid $(CO_2)_{12}H_6Cr_2$ or $H_3(CO_2)_6Cr{\cdot}Cr(CO_2)_6H_3$.

Potassium antimony oxalate, $(CO_2)_6K_2Sb.6Aq$, obtained by dissolving precipitated Sb_4O_6 in hydropotassium oxalate, is used in fixing certain colours.

Silver oxalate, $(CO_2Ag)_2$, is obtained as a white precipitate when silver nitrate is added to an oxalate. It explodes slightly when heated, leaving metallic silver.

Manganese oxalate, $(CO_2)_2Mn$, is used for mixing with drying-oils.

Oxidising-agents easily convert oxalic acid into water and CO_2; if a hot solution of the acid be poured on manganese dioxide, brisk effervescence is caused by the CO_2 produced. A similar result ensues if manganese dioxide be added to the mixture of an oxalate with dilute sulphuric acid. Nascent hydrogen reduces oxalic acid to glycollic acid; $(CO_2H)_2 + H_4 = CH_2(OH)\cdot CO_2H + H_2O$.

386. *Malonic acid*, $CH_2(CO_2H)_2$, is prepared from chloracetic acid, $CH_2Cl\cdot CO_2H$, by converting it into the potassium salt, and boiling this with potassium cyanide, when *potassium cyanacetate*, $CH_2(CN)\cdot CO_2K$, is formed. This is boiled with potash, which converts it into potassium malonate; $CH_2(CN)\cdot CO_2K + H_2O + KOH = CH_2(CO_2K)_2 + NH_3$. The excess of potash is neutralised by HCl, and calcium chloride added, which precipitates calcium malonate; by boiling this with the molecular proportion of oxalic acid, the calcium is left as oxalate, and the solution deposits tabular crystals of malonic acid. It fuses at 132° C. and afterwards decomposes into CO_2 and acetic acid; $CH_2(CO_2H)_2 = CO_2 + CH_3\cdot CO_2H$. It will be remembered that oxalic acid is decomposed into CO_2, and formic acid, $H\cdot CO_2H$.

Calcium malonate, like the oxalate, is very slightly soluble in water, and is found in the sugar beet; the silver and lead salts are insoluble. Malonic acid is found among the products of oxidation of allylene, amylene, and propylene with potassium permanganate.

The other acids of the malonic acid type are alkyl substitution derivatives of malonic acid, and may be built up therefrom by the treatment of its ethereal salts first with a sodium alkyloxide and then with an alkyl iodide. The series of reactions and their import has been given at p. 587.

Methylmalonic acid, $CH_3\cdot CH(COOH)_2$, is *ethylidene succinic acid*, isomeric with succinic acid, which is an ethylene derivative; hence it is called *isosuccinic acid*. It is prepared by hydrolysis of α-cyanopropionic acid, and from ethyl sodiomalonate and methyl iodide (see above). It should also be obtainable by treating ethylidene bromide, $CH_3\cdot CHBr_2$, with KCN and hydrolysing the cyanide, but this leads to ordinary succinic acid. It melts at 130° C., and decomposes into CO_2 and propionic acid.

387. **Succinic acid**, $C_2H_4(CO_2H)_2$, is *ethylene succinic acid*, and occurs ready formed in amber, from which it was originally obtained by distillation. It is prepared by the fermentation of tartaric acid, which may be regarded as dihydroxysuccinic acid, $C_2H_2(OH)_2(CO_2H)_2$, and becomes reduced to succinic acid.

The tartaric acid is neutralised with ammonia, largely diluted, and mixed with a little potassium phosphate, magnesium sulphate, and calcium chloride, to afford mineral food for the bacteria, which soon grow if the liquid be kept warm (25°–30° C.). The flask should be loosely closed to exclude air. After about two months, the ammonium tartrate has become ammonium succinate and carbonate; it is boiled to expel the latter, milk of lime added, and again boiled as long as NH_3 is expelled; the calcium succinate is decomposed by a slight deficiency of dilute H_2SO_4, the liquid filtered from the $CaSO_4$ and evaporated.

Succinic acid crystallises in prisms, which require about 20 parts of cold and 3 parts of hot water to dissolve them. It dissolves in alcohol but sparingly in ether. When heated, it emits vapour at 120° C., fuses at 185°, and at 235° distils as water and *succinic anhydride*, $C_2H_4(CO)_2O$; the vapours provoke coughing in a remarkable way, thus affording a test for the acid. It is very stable, and little affected by oxidising-agents. Fusion with KOH converts it into carbonate and propionate; $C_2H_4(CO_2H)_2 + 3KOH = CO(OK)_2 + C_2H_5\cdot CO_2K + 2H_2O$.

Calcium succinate, $C_2H_4(CO_2)_2Ca.3Aq$, is somewhat sparingly soluble in water: it occurs in the bark of the mulberry-tree. *Basic ferric succinate*, $Fe'''_2(C_4H_4O_4)''_2(OH)'_2$, is precipitated when ferric chloride is added to a succinate; it has a rich brown colour, and its production forms a good test for succinic acid, and is useful in quantitative analysis for separating Fe from Mn and some other metals.

Malic acid is *hydroxysuccinic acid*, and is also reduced by fermentation to succinic acid. Both malic and tartaric acid are reduced to succinic acid by the action of hydriodic acid. Succinic acid has been obtained synthetically by boiling ethene dibromide with potassium cyanide dissolved in alcohol, and boiling the ethene cyanide thus obtained with KOH dissolved in alcohol.

$$C_2H_4Br_2 + 2KCN = C_2H_4(CN)_2 + 2KBr; \text{ and}$$
$$C_2H_4(CN)_2 + 2KOH + 2H_2O = C_2H_4(CO_2K)_2 + 2NH_3.$$

Succinic acid is always produced in small quantity in the fermentation of sugar, and is therefore always present in beer, wine and vinegar. It is also produced when nitric acid oxidises fatty acids containing four or more carbon atoms. It occurs in unripe grapes, whilst ripe grapes contain tartaric (dihydroxysuccinic) acid. It is found in several plants, such as lettuce, poppies, and wormwood, and in certain lignites. It has also been found in the urine of the horse, goat, and rabbit.

When electrolysed, succinic acid yields C_2H_4, CO_2, and H, as might be expected from its formula, $C_2H_4(CO_2H)_2$.

Methylsuccinic acid, $COOH{\cdot}CH(CH_3){\cdot}CH_2{\cdot}COOH$, is also called *pyrotartaric acid* because it is formed by distilling tartaric acid (mixed with powdered pumice to diffuse the heat). The distillate is mixed with water, filtered, evaporated on the water bath and crystallised from alcohol. It is formed from propene as succinic acid is from ethene, and crystallises in prisms which melt at 112° C. and decompose into water and the anhydride. Having an asymmetric carbon atom it occurs in stereoisomeric forms.

Glutaric acid, $COOH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, isomeric with pyrotartaric acid (and with ethylmalonic acid and dimethylmalonic acid) melts at 97° C., and is obtained from trimethylene bromide (p. 539) through the KCN reaction. It yields an anhydride when heated.

The higher acids of this series do not yield anhydrides; the chief are:

Adipic, $C_4H_8(COOH)_2$,	from oxidation of oleic acid;	m.-p.	153° C.
Pimelic, $C_5H_{10}(COOH)_2$,	„ „ „ „ „	„	105° C.
Suberic, $C_6H_{12}(COOH)_2$,	„ „ „ cork	„	140° C.
Azelaic, $C_7H_{14}(COOH)_2$,	„ „ „ castor oil	„	106° C.
Sebacic, $C_8H_{16}(COOH)_2$,	„ distillation of oleic acid	„	133° C.
Brassylic, $C_{11}H_{22}(COOH)_2$	from oxidation of erucic acid	„	114° C.
Rocellic, $C_{15}H_{30}(COOH)_2$,	„ *Rocella tinctoria*	„	132° C.

388. **Dibasic Acids from Olefine Hydrocarbons, $C_nH_{2n-4}O_4$.**—The acids of this series are unsaturated, like those of the acrylic series, and can therefore combine with two atoms of bromine to become dibromo-derivatives of the acids of the preceding class, or with two atoms of hydrogen to become the acids of that class. Conversely, acids of this series are obtained by treating with KOH the dibromo-acids of the succinic series.

The first member of the series has the formula $C_2H_2(CO_2H)_2$, and might obviously exist in two forms, $CO_2H{\cdot}CH : CH{\cdot}CO_2H$ and $CH_2 : C(CO_2H)_2$. There is insufficient evidence to show, however, that the two acids *fumaric* and *maleic*, both of which have the molecular formula $C_2H_2(CO_2H)_2$, are position isomerides; they appear rather to be stereoisomerides.

The acid $CH_2 : C(COOH)_2$, *methylenemalonic acid*, is known only in the form of its ethereal salts.

Fumaric acid, $C_2H_2(CO_2H)_2$, is obtained by heating malic acid at 150° C. as long as water distils over; $C_2H_3(OH)(CO_2H)_2 = C_2H_2(CO_2H)_2 + H_2O$. The residue is treated with cold water to extract unaltered malic acid and the fumaric acid is crystallised from hot water or alcohol. At 200° C. it partly sublimes undecomposed, and the rest decomposes into water and maleic anhydride. Heated with much water at 150° C., it is reconverted into malic acid. NaOH at 100° C. slowly converts it into sodium malate. Nascent hydrogen, from water and sodium-amalgam, converts it into succinic acid, $C_2H_4(CO_2H)_2$. Hydriodic acid effects the same change, iodine being liberated. The fumarates of barium, calcium, and lead are sparingly soluble. Silver fumarate is very insoluble, and explodes when heated. The alkali fumarates, when electrolysed, yield C_2H_2, CO_2, which forms a carbonate, and H, thus justifying the formula given for the acid. Fumaric acid is found in several plants, especially in fumitory, Iceland moss, truffles, and other fungi. Fumaric acid is not oxidised by boiling with nitric acid.

Maleic acid, isomeric with fumaric acid, is produced when malic acid is quickly distilled. It is crystalline, melts at 130° C. and is easily decomposed by heat into water and maleic anhydride. It differs from fumaric acid by its ready solubility in cold water, by the solubility of its barium and calcium salts, and by its

unpleasant taste. It is converted into fumaric acid if heated in a sealed tube at 200° C., or if boiled with dilute acids.

In order to represent the isomerism between fumaric and maleic acid, it is supposed that the CO_2H groups are differently situated with regard to a plane drawn through the two nucleal carbon atoms of the molecule. On the plane of the paper, the supposed difference may be represented by the formulæ $\begin{matrix} H\cdot C\cdot CO_2H \\ \vdots\vdots \\ H\cdot C\cdot CO_2H \end{matrix}$ and $\begin{matrix} H\cdot C\cdot CO_2H. \\ \vdots\vdots \\ CO_2H\cdot C\cdot H \end{matrix}$ The first of these two formulæ is called the *plane-symmetrical*, or *cis-cis*-formula, whilst the second is called the *axial-symmetrical*, *centri-symmetrical*, or *cis-trans*-formula.

Since maleic acid very easily forms an anhydride, $\begin{matrix} H\cdot C\cdot CO \\ \vdots\vdots \\ H\cdot C\cdot CO \end{matrix}\!\!>\!O$ it may be supposed to have the first formula, because the formation of an anhydride would occur the more easily the greater the proximity of the CO_2H groups.* Many cases of stereoisomerism among ethylenic derivatives (*cf.* pseudo-butylene and crotonic acid) are believed to be explicable by formulæ resembling those given above, so that the expressions *maleinoid* and *fumaroid* structure are used.†

The main argument in favour of this view of the structure of the fumaric and maleic molecules is that the former yields racemic acid and the latter mesotartaric acid, by oxidation with $K_2Mn_2O_8$. Comparison of the above formulæ with those for racemic and mesotartaric acids on p. 622 shows that the acid having the cis-cis-formula would be the more likely to yield mesotartaric acid than the other acid would, because in mesotartaric acid both H atoms are on one side of the central plane.

By grouping the H and COOH groups at the four solid angles of the two tetrahedra represented in the middle diagram of Fig. 257, so as to produce the plane and axial symmetry of the above formulæ, some idea of the possible stereo-formulæ of maleic and fumaric acids may be obtained. Ingenious arguments have been advanced to explain the conversion of the one acid into the other by supposing that, by addition of elements, the double linking is opened up, so as to produce the left hand diagram of Fig. 257, the tetrahedra of which then rotate on their common axis, and, losing the added elements, again assume the form of the middle diagram: but this time the COOH and H groups would have assumed the opposite symmetrical relationship to that which they had before. Such arguments are open to well-found contradiction and cannot be detailed here

Citraconic (m.-p. 91° C.) and *mesaconic* (m.-p. 202° C.) *acids*, $C_3H_4(COOH)_2$, are homologues of fumaric and maleic acid, the former being *methylmaleic acid*, while the latter is *methylfumaric acid*. Thus they have the same relationship to each other as fumaric and maleic have. Citraconic acid, being the *cis*-form, yields an anhydride which is found in the products of destructive distillation of citric acid together with the anhydride of *itaconic acid* (m.-p. 161° C.), another isomeride which is *methylene succinic acid*, $COOH\cdot CH_2\cdot C(:CH_2)\cdot COOH$; hence these acids were formerly termed *pyrocitric acids*. If citraconic acid be heated for some time with dilute HNO_3 or strong HCl, it is converted into mesaconic acid. Mesaconic dissolves in about 40 parts of cold water, itaconic in about 20 parts, and citraconic in 1 part. All three are reduced by nascent H to pyrotartaric acid. They combine with the haloid acids to form isomeric substitution-products of pyrotartaric acid.

389. Of the **dibasic acids from the acetylene hydrocarbons**, *acetylene dicarboxylic acid*, $CO_2H\cdot C:C\cdot CO_2H$, need alone be noticed. It is produced by heating dibromosuccinic acid, $C_2H_2Br_2(CO_2H)_2$, with alcoholic potash, whereby 2HBr are removed. It crystallises with $2H_2O$, and decomposes when fused.

* Compare the ease with which 1:2 – phthalic acid yields an anhydride (p. 617).

† The special term *alloisomerism* or *geometrical isomerism* has been applied to these cases: it is not necessary.

390. **Dibasic Acids from Aromatic Hydrocarbons.**—These are obtained by oxidising benzene hydrocarbons containing side-chains. Thus, the most important of them, the three *phthalic acids*, $C_6H_4(COOH)_2$, can be prepared by oxidising the three xylenes, $C_6H_4(CH_3)_2$, and indeed most other disubstituted benzenes in which carbon is attached directly to the nucleus.

1 : 2-**phthalic acid** is the most important isomeride and is characterised by yielding an anhydride when heated, owing, no doubt, to the fact that the COOH groups are in the adjacent position. It is made in large quantity, for the manufacture of dye-stuffs, by oxidising naphthalene with strong H_2SO_4 in presence of mercury.

On a small scale naphthalene tetrachloride is oxidised with HNO_3. 1 part of $C_{10}H_8$ is carefully mixed, on paper, with 2 parts, by weight, of $KClO_3$, and added, *in small portions*, to 10 parts of strong HCl. The naphthalene tetrachloride, $C_{10}H_8Cl_4$, thus formed, is washed with water till free from acid, and allowed to dry. It is introduced into a flask and treated with strong HNO_3 (sp. gr. 1.45), which must be very gradually added, amounting to ten times the weight of naphthalene taken. The mixture is heated till all is dissolved, the nitric acid boiled off, and the residue distilled, when *phthalic anhydride* distils over and is converted into phthalic acid by dissolving in hot water and crystallising ; $C_6H_4\begin{<}{CO}{CO}O + H_2O = C_6H_4\begin{<}{COOH}{COOH}$

Phthalic acid crystallises in rhombic prisms, which are easily fusible, and readily decomposed into water and the anhydride. It is sparingly soluble in cold water, but dissolves readily in hot water, in alcohol, and in ether ; with NH_3 and $BaCl_2$ it yields a precipitate of barium phthalate. When heated with lime to 340° C., it yields benzoate and carbonate of calcium. Chromic acid oxidises phthalic acid completely into CO_2 and H_2O.

1 : 3-*Phthalic acid* or *isophthalic acid* crystallises in needles ; it is soluble in hot water, is not precipitated by $BaCl_2$ in presence of NH_3, and yields no anhydride when heated, but sublimes unchanged.

1 : 4-*Phthalic acid*, or *terephthalic acid*, is difficult to crystallise, and is insoluble in water, so that it is precipitated from its solutions in alkali by adding acid. The barium salt is sparingly soluble. The acid sublimes unchanged.

These differences in the properties of the three phthalic acids are of importance, since the production of one or other of the acids frequently serves to decide the constitution of a benzene derivative.

Phthalic anhydride crystallises in long prisms, m.-p. 128° C.; b.-p. 284° C. It is used in making eosin dyes.

By treating the phthalic acids with nascent hydrogen a large number of hydrogen-addition products, *hydrophthalic acids*, *e.g.*, $C_6H_4{\cdot}H_4{\cdot}(COOH)_2$, has been obtained. These are remarkable for the numerous cases of isomerism which they exhibit ; the cause of this has been traced, first, to the existence of *cis*- and *trans*-forms, as in the case of maleic and fumaric acids, and secondly, to the different positions of the double linking between the carbon atoms of the benzene nucleus, *e.g.*, the two dihydroterephthalic acids (*cf.* p. 550),

$$CO_2H{\cdot}C\begin{<}{CH_2{\cdot}CH}{CH{\cdot}CH_2}C{\cdot}CO_2H \text{ and } CO_2H{\cdot}C\begin{<}{CH_2{\cdot}CH_2}{CH{\cdot}CH}CO_2H.$$

Naphthalic acids are diabasic acids from naphthalene, $C_{10}H_6(CO_2H)_2$; six out of ten possible isomerides are known.

391. **Dibasic Hydroxy-acids.**—These may be regarded as oxidation products of diprimary polyhydric alcohols, or, in the case of those containing a benzene nucleus, as dicarboxylic acids from phenols.

Tartronic or *hydroxymalonic acid*, $CH(OH)(CO_2H)_2$, is formed by the action of nascent hydrogen on mesoxalic acid (*see below*), which is a product of the oxidation of uric acid. Its crystals melt at 158° C. and are then decomposed into water, CO_2, and an amorphous polymer of glycolide (p. 604). Tartronic acid was first

obtained by heating solution of dinitrotartaric acid; $C_2H_2(ONO_2)_2(CO_2H)_2 = CH(OH)(CO_2H)_2 + N_2O_3 + CO_2$. It is also formed when glucose is oxidised by an alkaline cupric solution, and when glycerine is oxidised by $K_2Mn_2O_8$. Barium tartronate, from which the acid is readily obtained, may be prepared by heating glyoxalic acid with potassium cyanide and baryta-water—

$$CHO{\cdot}CO_2H + KCN + Ba(OH)_2 + HOH = CH(OH)(CO_2)_2Ba + KOH + NH_3$$

Mesoxalic acid is regarded by some as *dihydroxymalonic acid*, $C(OH)_2(CO_2H)_2$, but since this compound contains two OH groups attached to one carbon atom, it is more probable that the acid is a ketonic acid of the form $CO(CO_2H)_2 + H_2O$, a view supported by the fact that it forms a compound with $NaHSO_3$, and combines with hydroxylamine (see *Ketones*). It is best obtained by boiling alloxan (*q.v.*) with baryta water. It crystallises in deliquescent prisms with $1H_2O$, and melts without loss of water at 115° C.

Malic, or Hydroxysuccinic acid, $COOH{\cdot}CH_2{\cdot}CHOH{\cdot}COOH$, is one of the chief natural vegetable acids, occurring in apples, gooseberries, currants, &c. It will be noted that its alcoholic C atom is asymmetric, hence it is known in the usual three optically isomeric forms. Strong solutions of the natural acid are dextro-rotatory, though when diluted they are lævo-rotatory. It is extracted from the juice of the unripe berries of the mountain ash.

The juice is boiled, filtered, nearly neutralised with milk of lime, and boiled, when *calcium malate*, $C_2H_3(OH)(CO_2)_2Ca.Aq$, is precipitated in minute crystals. This is dissolved to saturation in hot nitric acid diluted with ten times its weight of water. On cooling, crystals of *hydrocalcium malate*, $[C_2H_3(OH)(CO_2H){\cdot}CO_2]_2Ca.8Aq$, are deposited. These are dissolved in hot water, and decomposed by lead acetate, when lead malate is precipitated; this is suspended in water, and H_2S passed, when PbS remains precipitated, and malic acid is found in solution, from which it crystallises, though not very readily, in tufts of deliquescent needles.

The acid melts at 100° C. and at a higher temperature yields a feathery sublimate of maleic and fumaric acids and of maleic anhydride. Oxidation with chromic acid converts it into malonic acid, fusion with potash into oxalate and acetate. Hydriodic acid reduces it to succinic acid:

$$C_2H_3(OH)(COOH)_2 + 2HI = C_2H_4(COOH)_2 + H_2O + I_2.$$

By boiling bromosuccinic acid, $C_2H_3Br(COOH)_2$, with AgOH (silver oxide and water) the Br is exchanged for OH and inactive malic acid is produced. The *d*- and *l*-acids are obtained by reducing the tartaric acids (*q.v.*), of corresponding activity, with HI.

The active forms are also separated by crystallising the cinchonine salt of the inactive acid (*cf.* p. 606).

Some of the salts of malic acids also occur in nature. Cherries and rhubarb contain *acid potassium malate*, $C_2H_3(OH)(CO_2H)(CO_2K)$, while tobacco contains acid calcium malate. Normal calcium malate is less soluble in hot water, and is therefore precipitated on neutralising the acid with lime-water and boiling. *Lead malate* forms a white precipitate containing 3Aq., distinguished by fusing under water to a gummy mass, becoming crystalline on cooling.

392. **Tartaric or dihydroxysuccinic acid,** $CO_2H{\cdot}CHOH{\cdot}CHOH{\cdot}CO_2H$, is one of the most important vegetable acids, being often found in fruits associated with malic acid. It is prepared from *argol* or *tartar*, a crude form of acid potassium tartrate, $C_2H_2(OH)_2(COOH)(COOK)$, deposited in crystalline crusts during the fermentation of grape-juice.

This (45 ounces) is boiled with (2 gallons) water, and neutralised by adding (12½ ounces) powdered chalk, which converts the hydropotassium tartrate of the argol into calcium tartrate and potassium tartrate—

$$2C_4H_4O_6KH + CaCO_3 = C_4H_4O_6K_2 + C_4H_4O_6Ca + H_2O + CO_2.$$

The potassium tartrate dissolves and the calcium tartrate precipitates. Solution of calcium chloride (13½ oz. dissolved in 2 pints of water) is then added, to precipitate the potassium tartrate as calcium tartrate; $C_4H_4O_6K_2 + CaCl_2 = C_4H_4O_6Ca + 2KCl$. The calcium tartrate is strained off, washed, and heated for half an hour with dilute sulphuric acid (13 fluid ounces of acid in 3 pints of water), when calcium sulphate remains undissolved, and tartaric acid may be crystallised by evaporating the filtered solution; $C_4H_4O_6Ca + H_2SO_4 = C_4H_4O_6H_2 + CaSO_4$. The crude acid is dissolved in water, decolorised by animal charcoal, and again crystallised. A little sulphuric acid is generally added to promote the formation of large crystals. These often contain lead derived from the evaporating pans.

Properties of tartaric acid.—The crystals are monoclinic prisms, very soluble in water, and fairly so in alcohol, but nearly insoluble in ether. When heated rapidly to 170° C. it fuses, and becomes an amorphous deliquescent mass of *metatartaric acid*, isomeric with it. At 145° C. it becomes *tartralic acid*, $C_8H_{10}O_{11}$, two molecules of the acid having lost a molecule of water; at 180° C. it yields *tartaric anhydride*, $C_8H_8O_{10}$. All these may be re-converted into tartaric acid by digestion with water. On further heating, it undergoes destructive distillation, yielding chiefly pyruvic and pyrotartaric acids, together with *dipyrotartracetone*, $C_8H_{12}O_3$, which has a peculiar odour, like that of burnt sugar, by which tartaric acid may be recognised.

Fused KOH converts tartaric acid into acetate and oxalate. Boiled with nitric acid, much of it is oxidised to oxalic acid. Distilled with sulphuric acid and MnO_2, or $K_2Cr_2O_7$, it yields formic acid and CO_2.

Natural tartaric acid is *dextro-rotatory* and when heated with HI, in strong aqueous solution, at 120° C., in a sealed tube, it is reduced to dextro-malic acid, which is again reduced to succinic acid—

$$C_2H_2(OH)_2(CO_2H)_2 + 2HI = C_2H_3(OH)(CO_2H)_2 \text{ (\textit{malic acid})} + H_2O + I_2.$$

And $$C_2H_3(OH)(CO_2H)_2 + 2HI = C_2H_4(CO_2H)_2 \text{ (\textit{succinic acid})} + H_2O + I_2.$$

Conversely, tartaric acid can be obtained by the treatment of dibromo-succinic acid with moist silver oxide.

393. SALTS OF TARTARIC ACID.—A distinguishing character of tartaric acid is the sparing solubility of the *acid potassium tartrate*, $HK_4H_4O_6$, which is precipitated in minute crystals when almost any potassium salt is added to tartaric acid, and the solution is stirred with a glass rod, when the precipitate attaches itself to the lines of friction. Commercially this salt is known as cream of tartar, and is prepared by re-crystallising argol from hot water, which dissolves $\frac{1}{15}$th of its weight, and only retains $\frac{1}{100}$th on cooling. It is nearly insoluble in alcohol, which precipitates it from the aqueous solution, and this explains its separation from the grape-juice, as the proportion of alcohol increases during the fermentation. It dissolves easily in acids and in alkalies, which convert it into normal tartrate, $K_2C_4H_4O_6$. When heated, it evolves the burnt-sugar odour, and leaves a black mass of charcoal and potassium carbonate (*salt of tartar*).

Sodio-potassium tartrate, $NaKC_4H_4O_6.4Aq$, *Rochelle* or *Seignette's salt*, is prepared by neutralising a boiling solution of sodium carbonate with cream of tartar, when it crystallises on cooling, in fine rhombic prisms. It is useful in medicine.

Calcium tartrate, $CaC_4H_4O_6.4Aq$, occurs in grapes and in senna leaves. It is sparingly soluble in water, and is precipitated when $CaCl_2$ is added to an ammoniacal solution of a tartrate. It is soluble in potash and in ammonium chloride.

Cupric tartrate, $CuC_4H_4O_6.3Aq$, is sparingly soluble in water, but dissolves in alkalies to a deep blue solution, in which two atoms of the alkali metal have displaced H_2. Such a solution is often used in analysis, as *alkaline cupric solution*, or *Fehling's test*. Tartaric acid behaves in a similar way with several other metals, retaining them in alkaline solutions when they would otherwise be precipitated as hydroxides; in the cases of Al and Fe, this is turned to account in analysis.

Silver tartrate, $Ag_2C_4H_4O_6$, is precipitated by silver nitrate from a normal tartrate; it dissolves in ammonia, and the solution deposits metallic silver when heated, the tartaric acid being oxidised to carbonic and oxalic acids. This is taken advantage of in some processes for silvering mirrors.

Potassium-antimonyl-tartrate, $K(SbO)C_4H_4O_6$, or *tartar emetic*, is prepared by boiling cream of tartar (6 oz.) with water (2 pints) and (5 oz.) antimonious oxide; $Sb_2O_3 + 2KHC_4H_4O_6 = 2KSbOC_4H_4O_6 + H_2O$. From the filtered solution, on cooling, the salt crystallises in rhombic prisms of the formula $2KSbOC_4H_4O_6.Aq$. It is soluble in three parts of hot water and in fifteen parts of cold water. The crystals lose their water of crystallisation at 100° C., and when heated over 200° the emetic loses the elements of another molecule of water, and becomes $KSbC_4H_2O_6$, which is reconverted into emetic by boiling with water.

When barium chloride is added to tartar-emetic, a precipitate is formed, according to the equation $2KSbOC_4H_4O_6 + BaCl_2 = Ba(SbOC_4H_4O_6)_2 + 2KCl$. By decomposing this barium salt with sulphuric acid, an acid solution is obtained, which soon deposits antimonious hydroxide, but if it be neutralised with potash before decomposition occurs, it yields tartar-emetic. Hence it would seem that the emetic is the potassium salt of the acid $H(SbOC_4H_4O_6)$ or $C_2H_2(OH)_2(CO_2)_2SbO{\cdot}H$, which is derived from tartaric acid by exchanging one atom of H in the $(CO_2H)_2$ for the monad radicle *antimonyl*, Sb‴O″. The emetic acid has been named *tartryl antimonious acid*, so that tartar-emetic would be *potassium tartryl antimonite*. Other tartryl-antimonites have been obtained. By dissolving Sb_2O_3 in tartaric acid, and adding alcohol, a crystalline precipitate of antimonyl tartrate, $(SbO)_2C_4H_4O_6$, is obtained, and this becomes tartar-emetic when boiled with normal potassium tartrate $(SbO)_2C_4H_4O_6 + K_2C_4H_4O_6 = 2KSbOC_4H_4O_6$. For the antimony in tartar-emetic arsenic or boron may be substituted.

When excess of Sb_2O_3 is boiled with solution of tartaric acid, and the liquid evaporated to a syrup, it deposits crystals of $H(SbO)C_4H_4O_6$, which is decomposed by water, and appears to be identical with the tartryl-antimonious acid.

394. *Stereoisomerism as illustrated by tartaric acid.*—When natural (dextro-) tartaric acid, is heated with about one-tenth of its weight of water, in a sealed tube at 175° C. for some 30 hours, in the apparatus shown in Fig. 275, it is converted into an inactive isomeride, *racemic acid*, which crystallises with $1H_2O$ in triclinic prisms, melts at 202° C. and is much less soluble in water than dextro-tartaric acid is. By precipitating as acid potassium tartrate, the unaltered tartaric acid remaining in the mother-liquor obtained in crystallising racemic acid, there is left in solution the acid potassium salt of another inactive acid, *mesotartaric acid*, which crystallises in rectangular tables (with $1H_2O$).*

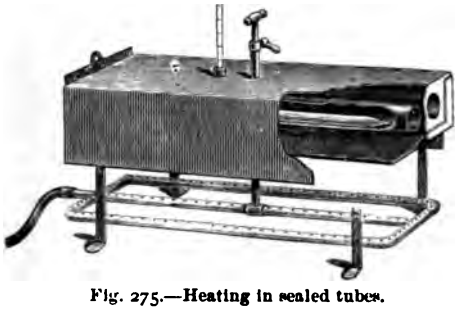


Fig. 275.—Heating in sealed tubes.

The differences between racemic and mesotartaric acid are sufficiently marked. The *acid potassium racemate* is more soluble than the tartrate, while the corresponding mesotartrate has not been crystallised. *Calcium racemate*, $CaC_4H_4O_6{\cdot}4Aq$, is less sparingly soluble than calcium tartrate and than *calcium mesotartrate*, $CaC_4H_4O_6{\cdot}3Aq$, so that calcium sulphate precipitates free racemic acid but neither of the other free acids. Calcium racemate is insoluble in ammonium chloride and

* For obtaining mesotartaric acid the sealed tube containing the tartaric acid and water should be heated at 165° C. for 2 hours.

in dilute acetic acid, which also fails to dissolve the mesotartrate ; the tartrate, however, is soluble in both.

Racemic acid is found mixed with the tartaric acid from certain samples of argol, and its crystals may be distinguished from those of tartaric acid by the cloudy appearance which they assume at 100° C. due to the loss of their water of crystallisation.

It has been found that racemic acid, like the inactive forms of other compounds containing an asymmetric carbon atom, can be split up by the methods referred to on p. 606 into the dextro-tartaric acid and *lævo-tartaric acid*, which is practically identical with the dextro-acid, save that it rotates the plane of polarisation to an equal extent to the left.

The classical researches of Pasteur on sodium-ammonium racemate are the foundation of stereochemistry.

The *sodium-ammonium racemate*, $NaNH_4C_4H_4O_6$, has the same crystalline form as the tartrate, but when formed at a temperature below 28° C. the crystals of the racemate differ from each other in the position of a certain unsymmetrical (*hemihedral*) face ; this is on the right hand in the one kind and on the left hand in the other (*enantiomorphous*). When these are picked out, and the acid extracted from them, the right-handed crystals yield ordinary dextro-rotatory tartaric acid, whilst the left-handed crystals yield lævo-tartaric acid. From a solution of cinchonine racemate, cinchonine lævo-tartrate separates first. The mould *penicillium glaucum* consumes dextro-tartaric acid in preference to the lævo-form when growing in racemic acid.

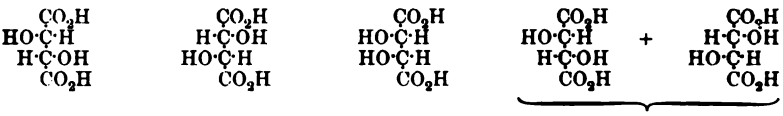
By mixing equal weights of dextro- and lævo-tartaric acid, heat is evolved and racemic acid is formed. So also calcium racemate is precipitated when solutions of the *l*- and *d*-calcium salts are mixed.

Three of the isomeric tartaric acids are thus accounted for, but the fourth,* mesotartaric acid, finds no analogue among the isomerides of compounds containing an asymmetric carbon atom so far considered. It is not capable of being split up into active components, nor is it produced by mixing the active forms. It is obtained practically pure by oxidising maleic acid with permanganate.

It is supposed that this fourth tartaric acid owes its existence to the fact that the molecule contains two asymmetric carbon atoms, so that it is possible for the one to have its groups arranged to give dextro-rotation while the groups of the other are arranged to give lævo-rotation. In this case the molecule would be *internally compensated* and would be optically inactive, just as the racemic acid molecule is *externally compensated*, consisting of two oppositely active molecules.

Tartaric acid belongs to the type of two tetrahedra having one solid angle in common (p. 535), and to the other solid angles of each tetrahedron there must be three different radicles, H, OH, CO_2H, attached. It is evident that these three radicles may be similarly or differently arranged around each tetrahedron. If they are similarly arranged, then it will be possible on severing the tetrahedra to place one inside the other, so that each solid angle shall correspond ; if they are differently arranged, this will not be possible. It is supposed that when the radicles are similarly arranged, the tartaric acid is either dextro- or lævo-rotatory, according as the arrangement is clockwise or anti-clockwise ; but if they are differently arranged, the dextro-rotatory power of one tetrahedron will annul the lævo-rotatory power of the other, and an inactive compound will result. The following figures will illustrate what has been said :

* A fifth acid, $CO_2H{\cdot}C(OH)_2{\cdot}CH_2{\cdot}CO_2H$, which contains two OH groups attached to the same carbon atom, has not been obtained.



Lævo-tartaric acid. | Dextro-tartaric acid. | Internally compensated or meso-tartaric acid. | Externally compensated tartaric acid. Racemic acid.

It is worthy of note that in whatever manner tartaric acid is synthesised the inactive forms are produced, and it is generally the case that artificial compounds are inactive whether they contain an asymmetric carbon atom or not. This is to some extent confirmatory of the foregoing theory ; for it would seem to be an even chance which way the groups arrange themselves round the asymmetric carbon atom, so that both forms are produced in equal amounts.

It is customary to speak of externally compensated compounds as *racemised compounds* and the passage of the active form into the externally compensated inactive, as *racemisation*. In many cases such racemisation occurs spontaneously under influences which are somewhat obscure, and the passage of an unstable active form into the more stable active form is known to occur.

395. **Saccharic acid**, $CO_2H{\cdot}[CHOH]_4{\cdot}CO_2H$, is obtained by oxidising sugar or starch with nitric acid, stopping short of the formation of oxalic acid. Sugar is heated with 3 parts of nitric acid of sp. gr. 1.3, till violent action begins. When no more red fumes are evolved, it is kept at 50° C. for some hours, diluted with two or three volumes of water, neutralised with K_2CO_3, and acidified strongly with acetic acid. On standing, *acid potassium saccharate*, $C_4H_8O_4(CO_2)_2HK$, crystallises. This is dissolved in a little potash, and precipitated by cadmium chloride. The precipitate of cadmium saccharate is suspended in water and decomposed by H_2S, the CdS filtered off, and the solution of saccharic acid evaporated. Saccharic acid forms a deliquescent amorphous mass, soluble in alcohol and in water. Its salts are somewhat similar to those of tartaric acid, the acid salts of potassium and ammonium being sparingly soluble. *Calcium saccharate*, $C_4H_8O_4(CO_2)_2Ca.Aq$, is crystalline, nearly insoluble in water, but soluble in acetic acid. The stereochemistry of saccharic acid will be noticed later.

Mucic acid, $CO_2H{\cdot}[CHOH]_4{\cdot}CO_2H$, stereoisomeric with saccharic, is prepared by oxidising gum arabic or milk sugar with nitric acid. Milk sugar is heated with 3 parts of nitric acid of sp. gr. 1.3 until red fumes are abundant ; the heat is then removed, when the acid separates as a granular powder sparingly soluble in water and alcohol. The mucates differ greatly from the saccharates, most of them being insoluble ; the acid potassium salt is more soluble than the normal salt. By boiling mucic acid with water for some time, it is converted into *paramucic acid*, which is isomeric with it, but more soluble in alcohol. Hydriodic acid reduces saccharic and mucic acids to *adipic acid*—

$$C_4H_8O_4(CO_2H)_2 + 8HI = C_4H_8(CO_2H)_2 + 4H_2O + 4I_2.$$

Pyromucic acid, or *furfurane α-monocarboxylic acid*, $C_4H_3O{\cdot}CO_2H$, is a product of the distillation of mucic acid, and may also be obtained by boiling furfural (pyromucic aldehyde, p. 586) with silver oxide and water. It forms prismatic crystals sparingly soluble in cold water, soluble in hot water, alcohol, and ether. It may be sublimed. The pyromucates are very soluble.

Meconic acid, $CO\langle^{CH = C(CO_2H)}_{C(OH):C(CO_2H)}\rangle O$, *hydroxypyrone dicarboxylic acid*, is extracted from opium by digesting it with hot water, neutralising the solution with calcium carbonate, and adding calcium chloride, which precipitates *acid calcium meconate*, $HCaC_7HO_7.Aq$, from which meconic acid may be crystallised by dissolving it in hot dilute HCl. It crystallises (with $3H_2O$) in plates, dissolving rather sparingly in cold water and ether, easily in hot water and alcohol. When heated, it loses CO_2, and becomes *comenic acid*, $C_6H_4O_5$, and when further heated, *hydroxypyrone* (*pyrocomenic acid*) $C_5H_3(OH)O_2$. Solution of meconic acid gives a fine red colour with ferric chloride, not bleached by mercuric chloride. With silver nitrate, it gives a white precipitate of *hydrodiargentic meconate*, $HAg_2C_7HO_7$, but if a drop of ammonia be added, and the liquid boiled, the precipitate becomes bright yellow *normal silver meconate*, $Ag_3C_7HO_7$. Meconic acid is closely related, by

its composition, to *chelidonic acid*, $C_7H_4O_6$, an acid obtained from celandine (*Chelidonium majus*), which belongs to the same botanical order as the opium poppy, which yields meconic acid.

396. **Polybasic acids.**—Very few of these are of any importance. *Tricarballylic acid*, $CH_2(CO_2H)\cdot CH(CO_2H)\cdot CH_2(CO_2H)$, may be obtained by heating citric acid with hydriodic acid. It may also be built up from glycerol, $C_3H_5(OH_3)$, by first converting this into allyl tribromide, $C_3H_5Br_3$ (p. 636), and heating the tribromide with alcohol and potassium cyanide to obtain *tricyanhydrin*, or *allyl tricyanide*, $C_3H_5(CN)_3$, which yields potassium tricarballylate and ammonia when boiled with potash; $C_3H_5(CN)_3 + 3KOH + 3H_2O = C_3H_5(CO_2K)_3 + 3NH_3$.

The calcium salts of tricarballylic, citric, and aconitic acids occur in the deposit formed in the stills of beet-sugar manufactories. Tricarballylic acid melts at 165° C. and crystallises in rhombic prisms, which are easily soluble in water and alcohol.

397. **Citric acid,** or *hydroxytricarballylic acid*, $CH_2(CO_2H)\cdot C(OH)(CO_2H)\cdot CH_2(CO_2H)$, **the most important polybasic acid, is found in many fruits, associated with malic and tartaric acid. The potassium and calcium salts are present in many vegetables and in the indigo and tobacco plants. The acid is prepared from lemon juice**

The juice is heated and chalk is added as long as effervescence occurs; this precipitates part of the acid as calcium citrate, leaving the rest in solution as an acid salt: this is precipitated by adding milk of lime, and boiling. The calcium citrate is washed with boiling water, decomposed by exactly the required quantity of dilute sulphuric acid, the liquid filtered from the calcium sulphate, and evaporated to crystallisation. It is sometimes recommended to ferment the lemon-juice with yeast for two days, and to filter before adding the chalk.

It is said that the acid can also be obtained industrially by fermenting glucose with a particular fungus.

The synthesis of citric acid from acetone is by the following steps:—(1) Acetone treated with chlorine yields *dichloracetone*, $CH_2Cl\cdot CO\cdot CH_2Cl$, which (2) heated with strong HCN yields *dichloracetone cyanhydrin*, $CH_2Cl\cdot C(OH)(CN)\cdot CH_2Cl$; on (3) hydrolysis this gives *dichloracetonic acid*, $CH_2Cl\cdot C(OH)(CO_2H)\cdot CH_2Cl$. (4) The two Cl atoms are now exchanged for CN by treatment with KCN, *dicyanoacetonic acid* being produced, $CH_2CN\cdot C(OH)(CO_2H)\cdot CH_2CN$, which (5) by hydrolysis yields citric acid.

Citric acid crystallises in rhombic prisms (with $1H_2O$) very soluble in water and fairly so in alcohol, but little in ether; they melt at 100° C., become anhydrous at 130°, and then melt at 153°. Further heated to 175°, the acid loses water and becomes *aconitic acid*, $C_3H_3(CO_2H)_3$.

By further heating, the aconitic acid becomes aconitic anhydride which then loses CO_2 and passes into the anhydride of *itaconic acid* (*methylene succinic acid*) $(COOH)CH_2\cdot C(:CH_2)(COOH)$, which crystallises in the neck of the retort. The liquid portion of the distillate contains the anhydride of *citraconic acid* (*methyl maleic acid*) isomeric with itaconic, into which it is converted by heating its concentrated solution to 120° C. Oxidising agents convert citric acid into acetone and its derivatives. When dehydrated by phosphoric or sulphuric acid, it also yields acetone, together with CO and CO_2; $C_3H_4(OH)(CO_2H)_3 = 2CO_2 + CO + H_2O + CH_3\cdot CO\cdot CH_3$ (*acetone*). Fusion with potash converts it into acetate and oxalate—

$$C_3H_4(OH)(CO_2H)_3 + 4KOH = 2(CH_3\cdot CO_2K) + (CO_2K)_2 + 3H_2O.$$

Solution of citric acid, mixed with excess of lime-water, gives no precipitate in the cold, distinguishing it from tartaric and oxalic acid; but when heated, it deposits *calcium citrate*, $Ca_3(C_6H_5O_7)_2\cdot 4Aq$, which is more soluble in cold than in hot water, but it is insoluble in potash, which dissolves calcium tartrate; ammonium chloride and acetic acid dissolve it.

Magnesium citrate, $Mg_3(C_6H_5O_7)_2\cdot 14Aq$, is easily soluble in water; mixed with $NaHCO_3$, citric acid, and sugar, and rendered granular by moistening with alcohol and drying, it forms *effervescent citrate of magnesia*.

Ferric citrate, $Fe_2(C_6H_5O_7)_2\cdot 6Aq$, used in medicine, forms transparent red scales

prepared by dissolving ferric hydroxide in citric acid and evaporating. *Ferric-ammonio-citrate*, $Fe_2(NH_4)_3(C_6H_5O_7)_3$, is also used medicinally.

Aconitic acid, $CO_2H.CH : C(CO_2H)\cdot CH_2\cdot CO_2H$, a tribasic acid of the olefine series, is obtained by heating citric acid in a retort till oily drops appear in the neck, and extracting the mass with ether, which leaves the unaltered citric acid undissolved. On evaporating the ether, aconitic acid is left in small crystals, easily soluble in water and alcohol. It is distinguished from citric acid by not precipitating when boiled with excess of lime water. Aconitic acid is found in monkshood (*Aconitum napellus*), beet-root, and sugar-cane, and in some other plants.

398. *Trimesic acid*, or 1 : 3 : 5-*benzenetricarboxylic acid*, $C_6H_3(CO_2H)_3$, results from the oxidation of mesitylene; it sublimes.

Mellitic acid, $C_6(COOH)_6$, is a hexabasic acid of the aromatic series (for it yields benzene when distilled with lime), which occurs as its aluminium salt in a mineral *mellite* or *honey-stone*. It crystallises in fine silky needles.

ACIDS CONTAINING NITROGEN.—See *Ammonia Derivatives* and *Cyanogen Derivatives*.

IV. KETONES OR ACETONES.

399. The relationship between an aldehyde and a ketone has already been noticed (p. 580); both contain a CO group, attached in the former to a hydrocarbon radicle and a hydrogen atom, as $CH_3\cdot CO\cdot H$, and in the latter to two hydrocarbon radicles, as $CH_3\cdot CO\cdot CH_3$, *acetone*. Both may be regarded as formed from an acid, the aldehyde by substituting an H atom, the ketone by substituting a hydrocarbon radicle, for the OH of the COOH group. Thus both may be formed from the acid chloride, *e.g.*, $CH_3CO\cdot Cl$—the aldehyde by action of nascent hydrogen, the ketone by action of the sodium compound of a hydrocarbon radicle :—

$$CH_3\cdot CO\cdot Cl + HH = CH_3\cdot CO\cdot H + HCl$$
$$CH_3\cdot CO\cdot Cl + CH_3Na = CH_3\cdot CO\cdot CH_3 + NaCl.$$

It has already been shown (p. 568) that the ketones are, so to speak, the aldehydes of the secondary alcohols, into which they are converted by nascent hydrogen. For the formation of ketones from esters of ketonic acids see p. 644.

It was shown at p. 580 that the aldehyde of an acid can generally be obtained by distilling a mixture of a calcium salt of that acid with calcium formate. If calcium acetate is distilled with calcium formate, acetic aldehyde is produced—

$$(CH_3\cdot CO\cdot O)_2Ca + (H\cdot CO\cdot O)_2Ca = 2(CH_3\cdot CO\cdot H) + 2(CaO\cdot CO_2).$$

But if calcium acetate be distilled with calcium acetate—that is, by itself—the products will be acetone and calcium carbonate—

$$(CH_3\cdot CO\cdot O)_2Ca + (CH_3\cdot CO\cdot O)_2Ca = 2(CH_3\cdot CO\cdot CH_3) + 2(CaO\cdot CO_2).$$

Ketones are *simple* or *mixed* accordingly as the hydrocarbon radicles attached to the CO group are the same or different; thus, by distilling a mixture of calcium acetate and propionate, the mixed ketone *acetone-propione* is obtained—

$$(CH_3\cdot CO\cdot O)_2Ca + (C_2H_5\cdot CO\cdot O)_2Ca = 2(CH_3\cdot CO\cdot C_2H_5) + 2(CaO\cdot CO_2).$$

The ketones are less easily oxidised than the aldehydes; for instance, they do not reduce alkaline silver solutions. By more powerful oxidants they are generally converted into two acids, the rupture of the molecule occurring at the CO group. Thus, propione $C_2H_5\cdot CO\cdot C_2H_5$, yields propionic acid, $C_2H_5\cdot CO_2H$, and acetic acid, $CH_3\cdot CO_2H$.

As in the aldehydes, the CO group is unsaturated, so that the ketones yield a number of combinations similar to those obtained with the aldehydes. *Ketoximes*, $R_2C:NOH$, like the aldoximes from aldehydes, are formed by reaction of ketones with hydroxylamine.

The oximes show a number of cases of stereo-isomerism, most of them, both aldoximes and ketoximes, existing in a stable and an unstable (*labile*) modification. This has been explained by supposing that a difference exists in the relative positions of the radicles attached to the carbon and nitrogen respectively (*cf.* maleic and fumaric acids). This difference may be represented thus: $\begin{matrix} R\cdot C\cdot R' \\ \| \\ N\cdot OH \end{matrix}$ and $\begin{matrix} R\cdot C\cdot R' \\ \| \\ HO\cdot N \end{matrix}$ (in the aldehydes R' is H). This theory is supported by the fact that one of the two aldoximes nearly always loses water more easily than the other, showing that the H and OH are probably nearer to each other in this aldoxime than in its isomeride. The syllables *syn-* and *anti-* are used to distinguish the forms, the first being syn-RR'-oxime the second anti-RR'-oxime.

With phenylhydrazine the ketones yield hydrazones, $R_2C:N\cdot NHC_6H_5$. Ketones containing a methyl group combine with $NaHSO_3$ to form sodium hydroxysulphonates, *e.g.*, $(CH_3)_2\cdot C(OH)\cdot SO_3Na$. By the action of PCl_5, the O of the CO group is exchanged for Cl_2 forming chlorides of the type R_2CCl_2 in which the Cl_2 is easily exchanged for H_2 to form a secondary paraffin hydrocarbon.

From their constitution, the ketones must afford many cases of isomerism (metamerism); thus, propione and methyl-propyl ketone have the same ultimate composition; so have methyl-butyl and propyl-ethyl ketones; methyl-amyl ketone and butyrone form another pair. Moreover, each ketone of the acetic series is isomeric with the aldehyde of the acid following next in the series; thus, acetic ketone, $(CH_3)_2CO$, is isomeric with propionic aldehyde, $C_2H_5\cdot CO\cdot H$.

400. **Acetone**, or *dimethyl-ketone*, $CH_3\cdot CO\cdot CH_3$, or *pyro-acetic spirit*, is obtained among the products of distillation of wood (p. 566), and may be prepared by distilling the acetate of lead, calcium, or barium, the last yielding the purest product (see the above equation). The crude distillate is shaken with a saturated solution of $NaHSO_3$ and the crystalline compound thus formed (see above) is freed from the mother-liquor and distilled with sodium carbonate, when acetone distils over, mixed with water, which is removed by fused calcium chloride.

Acetone is a colourless fragrant liquid, of sp. gr. 0.80, and boiling at 56°.3 C. It is inflammable, burning with a luminous flame. It mixes with water, alcohol, and ether. On adding solid KOH to its aqueous solution, the acetone separates and rises to the surface. It is a good solvent for certain resins and camphors, and is also used for making chloroform, iodoform and sulphonal. It is not so powerful a reducing-agent as aldehyde, and does not reduce silver nitrate. When oxidised by $K_2Mn_2O_8$ or by $K_2Cr_2O_7$ and H_2SO_4 it yields acetic and carbonic acids—$CH_3\cdot CO\cdot CH_3 + O_4 = CH_3\cdot CO\cdot OH + CO(OH)_2$.

Acetone is formed when vapour of acetic acid is passed through a red-hot tube, and when starch, sugar, and many other organic bodies undergo destructive distillation. It occurs in the urine of diabetic patients.

When acted on by dehydrating agents, such as sulphuric or hydrochloric acid or quicklime, acetone loses the elements of water, and yields *condensation-products*, richer in carbon; thus, two molecules of $(CH_3)_2CO$, losing H_2O, give $(CH_3)_2C:CH\cdot CO\cdot CH_3$, *mesityl oxide*, a liquid smelling of peppermint, and boiling at 130° C. Three molecules of $(CH_3)_2CO$, losing $2H_2O$, yield $[(CH_3)_2:C:CH]_2CO$, *phorone*, a crystalline solid, smelling of geraniums, and boiling at 196° C., whilst the loss of another H_2O gives C_9H_{12}, *mesitylene* (p. 549).

Acetone peroxide, $(C_3H_6O_2)_2$, is formed by mixing concentrated solutions of H_2O_2 and acetone. It forms crystals, melting at 97° C., insoluble in water and explosive.

An important thio-derivative of acetone is obtained by heating a mixture of acetone and mercaptan with HCl.

$$(CH_3)_2CO + 2C_2H_5SH = (CH_3)_2C(SC_2H_5)_2 + H_2O.$$

This is known as *mercaptol* and when oxidised by permanganate it yields *sulphonal* (*acetonediethylsulphone*), $(CH_3)_2C(SO_2C_2H_5)_2$, an important soporific which crystallises well and melts at 126° C.

Methyl-ethyl ketone may be obtained by the reaction between acetyl chloride and zinc ethide: $2(CH_3{\cdot}CO{\cdot}Cl) + Zn(C_2H_5)_2 = 2(CH_3{\cdot}CO{\cdot}C_2H_5) + ZnCl_2$. It boils at 81° C., and is present in small proportion in commercial acetone. When oxidised, it yields only one acid, acetic: $CH_3{\cdot}CO{\cdot}C_2H_5 + O_3 = 2(CH_3{\cdot}CO{\cdot}OH)$.

Benzophenone or *diphenyl ketone*, $(C_6H_5)_2CO$, prepared by distilling calcium benzoate, forms stable prisms which melt at 46° C., and labile rhombohedra which melt at 26° C.; the labile changes into the stable form on addition of a trace of the latter. Benzophenone boils at 307° C.

Acetophenone, methyl-phenyl ketone, $CH_3{\cdot}CO{\cdot}C_6H_5$, from calcium acetate and benzoate, melts at 20° C., boils at 202° and is used as an hypnotic (*hypnone*).

Methyl-nonyl ketone, $CH_3{\cdot}CO{\cdot}C_9H_{19}$, is the chief constituent of *oil of rue*, from which it may be precipitated by $NaHSO_3$. It may be obtained artificially by distilling calcium acetate with calcium rutate (m.-p. 15°; b.-p. 225° C.).

Naphthyl-phenyl ketone, $C_{10}H_7{\cdot}CO{\cdot}C_6H_5$, forms a dibromide, which is useful in optical experiments, on account of its high refractive power.

401. **Ketone-alcohols, ketone-aldehydes, ketone-acids, diketones.**—It was shown at p. 574 that these compounds may be regarded as oxidation products of polyhydric alcohols containing a secondary alcohol group, which might be expected to become a ketonic group on oxidation (p. 568) while the primary alcohol group would yield the aldehyde or acid group. Thus from α-propylene glycol, $CH_3{\cdot}CHOH{\cdot}CH_2OH$, would be obtained the ketone-alcohol, $CH_3{\cdot}CO{\cdot}CH_2OH$, the ketone-aldehyde, $CH_3{\cdot}CO{\cdot}CHO$, and the ketone-acid, $CH_3CO{\cdot}COOH$, and from β-butylene glycol, $CH_3{\cdot}CHOH{\cdot}CHOH{\cdot}CH_3$, the diketone, $CH_3{\cdot}CO{\cdot}CO{\cdot}CH_3$. All these compounds share with the ketones and aldehydes a tendency to combine and to undergo nucleal condensation; hence many are of great value in synthetic chemistry as steps to more complex compounds.

Isomerides are distinguished as α- and β- &c., as indicated on page 596.

Ketone-alcohols or *ketols* are exemplified by *acetylocarbinol* or *acetol*, $CH_3{\cdot}CO{\cdot}CH_2OH$, which boils about 150° C. and is obtained by cautious oxidation of α-propylene glycol with bromine water. Several of the sugars are ketols.

Pyroracemic aldehyde, or *methyl glyoxal*, $CH_3{\cdot}CO{\cdot}CHO$, is the type of the ketone-aldehydes: it is a volatile yellow oil.

Pyroracemic acid or *pyruric acid*, $CH_3CO{\cdot}COOH$, is the typical α-ketonic-acid. It is obtained by the destructive distillation of tartaric or racemic acid (p. 619), as an oxidation product of ethylidene lactic acid, $CH_3{\cdot}CHOH{\cdot}COOH$, and by hydrolysing acetyl cyanide, $CH_3CO{\cdot}CN$. This last method, the hydrolysis of an acidyl cyanide, is a general one for preparing α-ketone-acids. It is a colourless liquid smelling of acetic acid, boiling about 167° C., and soluble in water. It shows most of the reactions of a ketone and an acid; in addition, it is a strong reducing-agent, reducing alkaline silver nitrate, probably because the CO group has COOH attached to it instead of the second hydrocarbon radicle of a ketone. Baryta water converts it into *uritic acid*, a dibasic aromatic acid. With nascent H it yields lactic acid.

Aceto-acetic acid, or *acetonecarboxylic acid*, $CH_3{\cdot}CO{\cdot}CH_2COOH$, is the typical β-ketone-acid, all of which are very unstable, tending to break down into CO_2, from the carboxyl group, and the corresponding ketone. Its ethyl salt (*see Ethereal Salts*) is more stable than the acid and is an important compound for synthetical work: by saponifying this salt potassium aceto-acetetate, and from this the free acid is obtained. It is a liquid soluble in water and decomposing into acetone and CO_2 when heated.

Lævulinic acid, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2COOH$, is the type of the γ-ketone-acids, which are also easily broken down by heat; but instead of losing CO_2 they lose H_2O, yielding γ-lactones (p. 607) from unsaturated hydroxy-acids. Thus, levulinic acid yields γ-*lactones* from angelic acid;

$$CH_3C:CH{\cdot}CH_2COO \text{ and } CH_2:C{\cdot}CH_2{\cdot}CH_2COO.$$

Levulinic acid is a product of the action of acids on various carbohydrates, especially levulose. It melts at 32·5° C. and boils at 239° C., dissolves in water and is used in calico-printing.

Phenylglyoxylic acid or *benzoyl formic acid*, $C_6H_5{\cdot}CO{\cdot}COOH$, is produced by oxidising mandelic acid and by hydrolysing benzoylcyanide. It melts at 65° C.

Diacetyl, $CH_3CO{\cdot}COCH_3$, is the simplest α-diketone.* It is made by heating *isonitrosomethylacetone*, $CH_3{\cdot}C(NOH){\cdot}CO{\cdot}CH_3$ with acid, and is a greenish-yellow liquid, smelling of quinine and boiling at 87° C. The β-diketones, like *acetylacetone*, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_3$, are remarkable for forming metallic salts (*acetylacetonates*), the true constitution of which is in doubt. The γ-diketones, like *acetonylacetone*, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3$, do not share this property, but are important because of the ease with which they pass into closed-chain compounds of the furfurane or pyrrol type (*q.v.*)

V. ETHERS.

402. The ethers are derived from the alcohols by the substitution of a hydrocarbon radicle for the hydrogen in the OH group; thus, if methyl alcohol, $CH_3{\cdot}OH$, be treated with Na, the hydroxl hydrogen is displaced by sodium, and $CH_3{\cdot}ONa$, or *sodium methoxide*, is obtained. If this be acted on by methyl iodide—$CH_3{\cdot}ONa + CH_3I = CH_3{\cdot}O{\cdot}CH_3 + NaI$—the H in CH_3OH is displaced by CH_3, and *methyl ether*, $CH_3{\cdot}O{\cdot}CH_3$, is formed. It will be evident that a similar reaction between sodium methoxide and ethyl iodide, C_2H_5I, would furnish the *mixed ether*, methyl-ethyl ether, $CH_3{\cdot}O{\cdot}C_2H_5$, so that the number of ethers obtainable would exceed that of the alcohols.

Just as the alcohols are comparable with the metallic hydroxides (p. 561), albeit far less prone to chemical change, so the ethers may be compared with the metallic oxides deprived of most of their chemical energy. This view is supported by a second general method of preparing them, namely, by heating the alkyl halides with metallic oxides, $2CH_3I + Ag_2O = (CH_3)_2O + 2AgI$; and by their reaction with hot hydriodic acid to yield an iodide and water, as the alkali oxides do—

$$K_2O + 2HI = H_2O + KI; \text{ and } (CH_3)_2O + 2HI = H_2O + 2CH_3I.$$

The usual method for obtaining the ethers is by the action of sulphuric acids on alcohols, as will be explained below.

The ethers are generally insoluble in water, and lighter and more volatile than the corresponding alcohols. They are almost as indifferent to reagents as the hydrocarbons are, and probably for a like reason, viz., that all the hydrogen is combined with carbon. The reaction of the ethers will be gathered from those of ethyl ether.

It will be remarked that the ethers derived from the alcohols of the series $C_nH_{2n+2}O$ form an homologous series isologous with the alcohols, that each ether is metameric with the isologous alcohol, and that the ethers containing an odd number of carbon atoms are mixed ethers.

* By the new system of nomenclature, ketones are named like the alcohols (see foot-note p. 568), *-on* being substituted for *-ol*. Thus, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$ is *2-pentanon* (the O being attached to the second C atom). $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_3$ is *2:4-pentanedion*.

Ethers.		Alcohols.	
Methyl . . .	$CH_3 \cdot O \cdot CH_3$	Ethyl . . .	$C_2H_5 \cdot OH$
Methyl-ethyl . .	$CH_3 \cdot O \cdot C_2H_5$	Propyl . . .	$C_3H_7 \cdot OH$
Ethyl . . .	$C_2H_5 \cdot O \cdot C_2H_5$	Butyl . . .	$C_4H_9 \cdot OH$
Ethyl-propyl . .	$C_2H_5 \cdot O \cdot C_3H_7$	Amyl . . .	$C_5H_{11} \cdot OH$
Propyl . . .	$C_3H_7 \cdot O \cdot C_3H_7$	Caproic . . .	$C_6H_{13} \cdot OH$

403. *Methyl ether*, or *dimethyl oxide*, $CH_3 \cdot O \cdot CH_3$, is a fragrant inflammable *gas* prepared by adding methyl alcohol (2 parts by weight) to cooled strong H_2SO_4 (3 parts) and heating to about 140° C., keeping up a supply of methyl alcohol, as in the preparation of ether (*q.v.*), the reaction being the same as in the preparation of ether, if methyl be written for ethyl. The gas may be stored for use by passing it into cooled H_2SO_4, which dissolves 600 volumes of it and gives it up again when mixed with water. It is condensed by cold or pressure to a liquid boiling at −21° C., and used for producing cold. Water absorbs about 37 times its volume of the gas.

404. **Ether**, or *sulphuric ether*, $C_2H_5 \cdot O \cdot C_2H_5$, is prepared by distilling alcohol with sulphuric acid. If two measures of alcohol be carefully added to one measure of strong sulphuric acid, and the mixture distilled, ether passes over together with water, and if alcohol be added from time to time, a small quantity of sulphuric acid suffices to etherify a large quantity of alcohol. The alcohol is first converted into hydrogen ethyl sulphate, *sulphethylic acid* or *ethylsulphuric acid*—

$$SO_2(OH_2) + C_2H_5 \cdot OH = SO_2(OH)(OC_2H_5) + HOH.$$

When this is heated to about 140° C. with more alcohol, it is decomposed into ether and sulphuric acid, which then acts in the same way upon a fresh quantity of alcohol—

$$SO_2(OH)(OC_2H_5) + C_2H_5 \cdot OH = C_2H_5 \cdot O \cdot C_2H_5 + SO_2(OH)_2.$$

Hence the process has been termed the *continuous etherification* process and is carried out in the following manner:—

Alcohol of sp.gr. 0.83 is carefully added, with continued shaking, to an equal volume of strong sulphuric acid, cooled in a vessel of water. When the mixture is cold, it is poured into a retort or flask (Fig. 276), which is connected with a reservoir of alcohol and a well-cooled condenser. The mixture is quickly heated till it boils, when its temperature will be about 140° C. (284° F.), and alcohol is then allowed to pass in slowly from a siphon tube furnished with a stop-cock, and dipping below the liquid in the flask; the temperature should remain as nearly as possible at 140° C., which will be the case if the rate of flow of the alcohol is so regulated as to keep the mixture at the same level. A thermometer is fixed in the cork with its bulb in the liquid. When the total quantity of alcohol used amounts to six or seven times that originally taken, the process must be stopped, because secondary reactions, attended by carbonisation, have used up much of the sulphuric acid. The liquid collected in the receiver contains about two-thirds of its weight of ether, with about one-sixth of water, an equal quantity of alcohol, and a little sulphurous acid. It usually separates into two layers, of which the upper is ether. The whole is introduced into a narrow stoppered bottle, and shaken with cold water, added in small portions, as long as the layer of ether on the surface increases in volume; a little potash is then added to fix SO_2, and, after shaking, the upper layer of ether is drawn off, by a siphon or separator, into a flask containing lumps of fused calcium chloride, to remove water and alcohol. After standing for some hours, the ether is distilled off in a water-bath at as low a temperature as possible. To free it entirely from water, it must be again rectified after digestion with powdered quick-lime, and finally with bright sodium, till no more hydrogen bubbles are visible. *Methylated ether* is prepared from *methylated spirit*, and is much cheaper than pure ether, for which it may often be substituted.

It has been found that benzene sulphonic acid ($C_6H_5SO_3H$) may advantageously be substituted for the sulphonic acid, as it will etherify about 100 times its weight

of alcohol. The acid is melted in the flask and alcohol run in slowly, the temperature being kept about 140° C. $C_6H_5SO_2C_2H_5$ is first formed and is decomposed by more alcohol into $C_6H_5SO_3H$ and $(C_2H_5)_2O$.

Theory of etherification.—The process described above for the preparation of ether had long been practised before a satisfactory explanation of it was arrived at. One of the earliest views regarded the formation of ether as a simple removal of water by the sulphuric acid from the alcohol, which was then believed to be a compound of ether and water; but against this it was urged that the water was not retained by the acid, but distilled over with the ether, and that the same acid would etherify

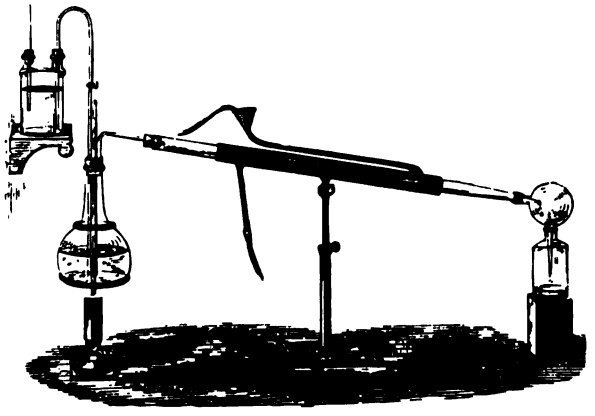


Fig. 276.—Continuous etherification.

successive additions of alcohol. Passing over the theory of *catalytic* action, or decomposition by contact, which was a mere statement of the facts without any real explanation, we come to the important observation that the first product of the action of sulphuric acid on alcohol is sulphethylic acid, which is decomposed, when distilled with more alcohol at 140°, into ether, water, and sulphuric acid, as in the equations given on p. 628.

Very strong evidence that the above equations represent the reactions occurring in the etherification process is furnished by the following experiment:—Amyl alcohol, $C_5H_{11}\cdot OH$, is converted by sulphuric acid into *sulphamylic acid*, $C_5H_{11}\cdot SO_4H$, which is heated in the flask (Fig. 276), whilst ethyl alcohol, $C_2H_5\cdot OH$, is allowed to flow in from the reservoir; this decomposes the sulphamylic acid, yielding sulphuric acid, and *amyl-ethyl ether*—

$$C_5H_{11}\cdot SO_4H + C_2H_5\cdot OH = C_5H_{11}\cdot O\cdot C_2H_5 + H_2SO_4.$$

If the process is continued after all the amyl-ethyl ether has passed over, only ethyl ether is obtained. In this manner any mixed ether can be prepared.

405. *Properties of ether.*—A very mobile colourless liquid with a characteristic odour; sp. gr. at 15° C. 0.70. It boils at −35° C., evaporates very rapidly in air, producing intense cold, and yielding a very heavy vapour, of sp. gr. 2.59, which is very inflammable, and renders ether dangerous in unskilled hands. It melts at 113° C. It is sparingly soluble in water, so that, when shaken with it, the ether generally rises to the surface on standing, rendering it very useful for collecting certain substances, such as bromine and alkaloids, from large bulks of aqueous

solutions into a small bulk of ether. Ten volumes of water dissolve one volume of ether. Thirty-four volumes of ether are required to dissolve one volume of water, so that ether, free from alcohol, could not contain much water, but commercial ether contains alcohol, which enables it to take up a larger quantity of water. Ether and alcohol may be mixed in all proportions, but the addition of much water generally brings the ether to the surface. Ether is much used in laboratories as a solvent, especially for fatty substances and alkaloids, and by the photographer in making collodion.

Ether containing water becomes turbid when shaken with CS_2 and that containing alcohol dissolves sufficient aniline violet to become coloured when shaken with this dye-stuff.

The properties of ether admit of some interesting experiments.

1. If a little ether be evaporated by blowing upon it in a watch-glass, with a drop of water hanging from its convexity, the water will be speedily frozen. A thin beaker containing ether may be frozen to a wet table by blowing into it with the bellows.

2. A piece of tow, wool, or sponge, wetted with ether, is placed at the upper end of a sloping trough or gutter of wood or metal, over six feet long; a match applied at the lower end fires the train of vapour.

3. A jug is warmed with a little hot water, emptied, and a little ether poured into it; the vapour may be poured into a row of small beaker-glasses, each of which is afterwards tested with a taper.

4. A pneumatic trough is filled with warm water, and a small test-tube filled with ether is inverted with its mouth under the water, and quickly decanted up into a gas-jar filled with warm water, when it will be vaporised, and may be decanted through the water into other vessels, and treated like a permanent gas. Some cold water poured over the jar containing it at once proves its condensable character.

406. Ether is also produced by the reactions given on p. 627, C_2H_5 being substituted for CH_3 in the equations. Ethyl iodide, heated with a small quantity of water, under pressure, yields, first alcohol, and afterwards ether—

$$C_2H_5I + HOH = C_2H_5{\cdot}OH + HI, \text{ and } C_2H_5I + C_2H_5{\cdot}OH = C_2H_5{\cdot}O{\cdot}C_2H_5 + HI.$$

Other acids besides sulphuric are able to produce ether from alcohol, especially those which are non-volatile and polybasic, such as phosphoric, arsenic, and boric, which probably act in the same way as sulphuric. But certain salts, such as zinc chloride and aluminium sulphate, also generate ether from alcohol, and the explanation of this is less simple. It will be found that such salts are capable of decomposition by water, with formation of basic salts and free acid; thus, $ZnCl_2 + HOH = ZnCl{\cdot}OH + HCl$, or $Al_2(SO_4)_3 + 4HOH = Al_2SO_4(OH)_4 + 2H_2SO_4$.

If these reactions occur with alcohol, $C_2H_5{\cdot}OH$, instead of with HOH, the products would be C_2H_5Cl instead of HCl, and $C_2H_5{\cdot}HSO_4$ instead of H_2SO_4, and either of these would react with the excess of alcohol to produce ether.

Ether may be converted into alcohol by heating it with water and a very little sulphuric acid, in a sealed tube, at 180° C. The ether is probably converted at first into sulphethylic acid, and this into alcohol and sulphuric acid, the etherification reaction (p. 628) being reversed.

When ether is acted on by hydriodic acid gas, in the cold, it yields alcohol and ethyl iodide; $(C_2H_5)_2O + HI = C_2H_5{\cdot}OH + C_2H_5I$. If a *mixed* ether, such as ethyl-amyl ether, be treated in this way, the radicle containing more carbon is the one converted into an alcohol; $C_2H_5{\cdot}O{\cdot}C_5H_{11} + HI = C_5H_{11}{\cdot}OH + C_2H_5I$.

Ordinary oxidising-agents convert ether into aldehyde and acetic acid. Ozonised oxygen converts it into formic, acetic, and oxalic acids and hydrogen peroxide.

When ether vapour is passed over heated potash, hydrogen, marsh gas, and potassium carbonate are formed, potassium acetate being probably produced in the first stage of its reaction; $(C_2H_5)_2O + 2KOH + H_2O = 2KC_2H_3O_2 + 4H_2$.

Ether enters into combination with several metallic chlorides and bromides, forming crystalline compounds; stannic chloride combines with two molecules of ether, forming $SnCl_4(C_4H_{10}O)_2$; aluminium bromide forms $Al_2Br_6(C_4H_{10}O)_2$.

Ether is inflamed by contact with chlorine; but if it be very well cooled, and

light be excluded, it yields a series of substitution-products. *Monochlorether*, *dichlorether*, and *tetrachlorether* are known. *Perchlorinated ether*, $C_4Cl_{10}O$, requiring sunlight for its formation, is a crystalline body (m.-p. 68° C.) smelling like camphor.

Distilled with PCl_5, ether yields C_2H_5Cl and $POCl_3$ but no HCl (*cf.* p. 579).

407. **Ethers from polyhydric alcohols.** — By treating monosodium glycol $C_2H_4(OH)(ONa)$ with C_2H_5I, as in the general reaction (p. 627), *monoethyl glycol ether*, $C_2H_4(OH)(OC_2H_5)$ (b.-p. 127° C.) is obtained. If disodium glycol be similarly treated, the *diethyl* ether $C_2H_4(OC_2H_5)_2$ (b.-p. 123° C.) is obtained.

Regarding the formation of an ether as the abstraction of HOH from the two OH groups of two molecules of an alcohol, glycol might be expected to form an internal ether, $\begin{matrix}CH_2\\ \cdot\\ CH_2\end{matrix}\!\!>\!O$. This compound, *ethylene oxide*, is produced when glycol chlorhydrin (p. 575) is distilled with potash :—

$$\begin{matrix}CH_2OH\\ \cdot\\ CH_2Cl\end{matrix} + KOH = \begin{matrix}CH_2\\ \cdot\\ CH_2\end{matrix}\!\!>\!O + KCl + HOH.$$

It is isomeric with ethyl aldehyde, boils at 12·5° C. and easily passes back into glycol derivatives. *Trimethylene oxide*, $CH_2\begin{matrix}CH_2\\ \cdot\\ CH_2\end{matrix}\!\!>\!O$, boils at 50° C. and is similarly prepared from the chlorhydrin of propylene glycol, $CH_2Cl{\cdot}CH_2{\cdot}CH_2OH$.

408. *Glycerine ether*, $C_3H_5{\cdot}O_3{\cdot}C_3H_5$, may be regarded as glycerine, $C_3H_5(OH)_3$, in which glyceryl, C_3H_5, has been substituted for the H_3 of the $(OH)_3$. It is formed when glycerine is distilled with $CaCl_2$, and is a colourless, inodorous liquid, boiling at about 170° C., and of sp. gr. 1.16; it mixes with water. Its behaviour with hydriodic acid is analogous to that of ethyl ether, for it is converted into glycerine and glyceryl tri-iodide, $C_3H_5I_3$.

409. **Aromatic Ethers.**—These may be either the true ethers corresponding with the aromatic alcohols, or ethers derived from phenols, which, it will be remembered, differ from the alcohols in having the OH group attached directly to the benzene nucleus.

Benzyl ether, $(C_6H_5{\cdot}CH_2)_2O$, is prepared by distilling benzyl alcohol with B_2O_3 which removes the elements of water, $2C_6H_5{\cdot}CH_2OH - HOH = (C_6H_5{\cdot}CH_2)_2O$. It is a colourless liquid not miscible with water, and boiling at 296° C.

Diphenyl oxide, or *phenyl ether*, $C_6H_5{\cdot}O{\cdot}C_6H_5$, obtained by distilling phenol with aluminium chloride, forms prisms, fusing at 28° C. and boiling at 252° C. It smells like the geranium leaf, and is remarkable for its stability under the influence of oxidising- and reducing-agents. Water does not dissolve it, but alcohol and ether do so.

Phenyl-methyl ether, $C_6H_5{\cdot}O{\cdot}CH_3$, is prepared by passing methyl chloride through sodium phenol at 200° C. It is a fragrant liquid, of sp. gr. 0.991, boiling at 152°. This ether is identical with *anisöil*, obtained by distilling anisic acid (p. 608) with baryta. Methyl salicylate, or winter green oil, $C_6H_4(OH){\cdot}CO_2{\cdot}CH_3$, is metameric with anisic acid, and also yields phenyl-methyl ether when distilled with baryta. Hydriodic acid heated to 140° C. with anisoïl, in a sealed tube, converts it into phenol and methyl iodide; $C_6H_5{\cdot}OCH_3 + HI = C_6H_5{\cdot}OH + CH_3I$.

This reaction is typical of the method commonly employed in determining the number of methoxy-groups (OCH_3) in the molecule of a compound. It is known as *Zeisel's method*, and consists in boiling a known weight (0.3 gram) of the substance with fuming hydriodic acid (10 c.c.) in a flask *A* (Fig. 277) through which a gentle current of CO_2 is passed. This carries the CH_3I water vapour and HI through the condensing-tube *B*, containing a number of aludels shown drawn to an enlarged scale at *C*. The temperature of the water-bath *D* is regulated to ensure that the distillation shall not be too rapid, which is indicated by the thermometer *E* marking a temperature of 50° C. The methyl iodide does not condense at this temperature and passes through the absorption flasks *F*, containing water and red phosphorus, where it leaves the HI and a little free I that it contains, and then into a wash bottle containing an alcoholic solution of silver nitrate. Here the methyl iodide is decomposed yielding a precipitate of AgI, which is collected, washed, and weighed. From its weight that of the CH_3I and therefore of the OCH_3 in the compound taken, is calculated.

The methyl ethers of the phenols are formed at the ordinary temperature when diazomethane, CH_2N_2, and a phenol are brought in contact, *e.g.*, $C_6H_5OH + CH_2N_2 = C_6H_5OCH_3 + N_2$. They are not changed when heated with alcoholic potash.

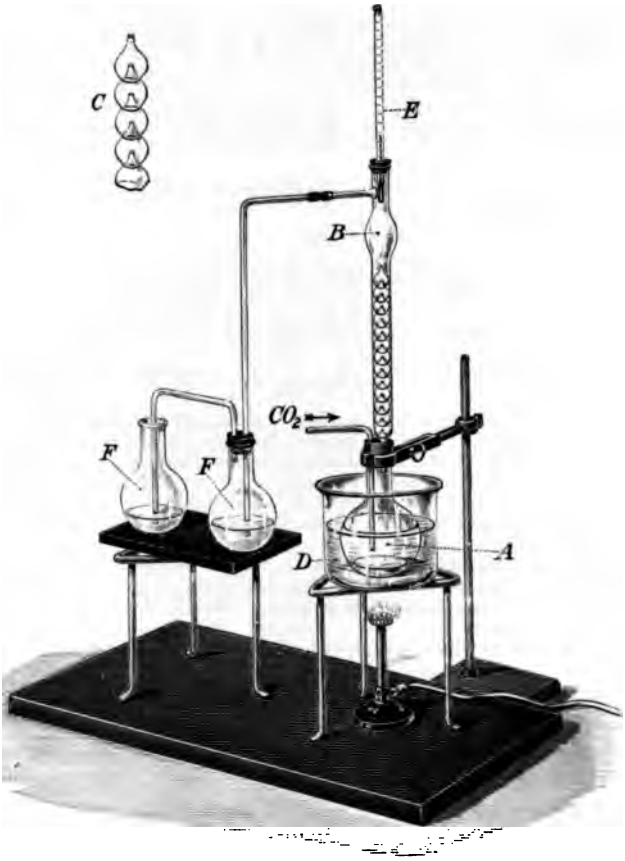


Fig. 277.—Apparatus for determining methoxyl groups.

Anethol, the camphor-like substance in oil of anise is 1 : 4-propenyl-anisoïl, $CH_3{\cdot}CH : CH{\cdot}C_6H_4{\cdot}OCH_3$; it melts at 22° C. and boils at 233° C.

Phenyl ethyl ether, $C_6H_5{\cdot}O{\cdot}C_2H_5$, or *phenetoïl* is obtained by distilling ethyl salicylate with baryta ; it boils at 172° C.

VI. HALOGEN DERIVATIVES.

410. **Halogen Compounds from Hydrocarbons.—(A) From open-chain hydrocarbons.**—It has been already noticed (p. 530) that these products result in many cases from the direct action of the halogens on the hydrocarbons, but whilst Cl and Br react thus by metalepsis with hydrocarbons, iodine seldom does so unless an absorbent for HI (*e.g.*, HgO) be present; this is because the metalepsis is a reversible reaction (p. 309), *e.g.*, $CH_4 + I_2 \rightleftarrows CH_3I + HI$.

Since the unsaturated hydrocarbons generally combine with the halogen to form addition products (p. 534), which are either identical or isomeric with the halogen substituted saturated hydrocarbons,* some other method must generally be resorted to in order to prepare halogen substitution-products of unsaturated hydrocarbons. Thus, they are obtained either by treating the halogen substituted saturated hydrocarbons with reagents which will remove halogen hydride, or by only partially saturating still more unsaturated hydrocarbons with halogen; *e.g.*, $C_2H_4Cl_2 - HCl = C_2H_3Cl$; $C_2H_2 + Cl_2 = C_2H_2Cl_2$.

The halogen substitution-products from all hydrocarbons are obtainable by the interaction of the alcohols with phosphorus halides, or, what is equivalent, with phosphorus and a halogen. Examples will be met with in the following pages. In a large number of cases the mere treatment of an alcohol with halogen hydride, particularly in the presence of a dehydrating agent, will produce the halogen substitution-product, the reaction being of the type $R{\cdot}OH + HX = RX + HOH$.

Methyl choride, or *monochloro-methane* CH_3Cl, is prepared by passing HCl gas into a boiling solution of zinc chloride in twice its weight of methyl alcohol, contained in a flask connected with a reversed condenser. The methyl chloride is evolved as a gas which may be washed with a little water to remove HCl, dried by passing over calcium chloride, and condensed in tubes cooled in a mixture of ice and calcium chloride crystals. The final result is expressed by the equation $CH_3OH + HCl = CH_3Cl + HOH$. The action of the zinc chloride is little understood. Methyl chloride is an inflammable gas of ethereal odour, liquefied by a pressure of $2\frac{1}{2}$ atm. at 0° C. Its boiling-point is − 24° C. Water dissolves 4 vols. of the gas and alcohol 35 vols.

Methyl chloride may also be prepared by distilling methyl alcohol with sodium chloride and sulphuric acid. It is made on a large scale, for use in freezing-machines, from the trimethylamine obtained by distilling the refuse of the beet-sugar factories: this is neutralised with hydrochloric acid, and heated to 260° C., when it is decomposed into trimethylamine, ammonia and methyl chloride; $3N(CH_3)_3HCl = 2N(CH_3)_3 + NH_3 + 3CH_3Cl$.

Methyl chloride is very stable; potash decomposes it with difficulty, yielding methyl alcohol and potassium chloride. It is used in the preparation of some of the aniline colours.

Ethyl chloride, or *monochlorethane,* C_2H_5Cl, is prepared by substituting ethyl for methyl alcohol in the foregoing prescription. The purified vapour is passed into 95 per cent. alcohol kept cool by water. The alcohol absorbs half its weight of ethyl chloride, which may be evolved from it by gently heating, and purified by passing through a little sulphuric acid. It is a fragrant liquid of sp. gr. 0.92 and boiling-point 12°.5 C. It is sparingly soluble in water, and burns with a bright flame edged with green. Ethyl chloride is formed when olefiant gas and HCl are heated together for some time.

Methyl bromide, CH_3Br, is prepared by acting upon methyl alcohol with phosphorus and bromine; $3CH_3OH + Br_2 + P = 3CH_3Br + P(OH)_3$. Four parts of methyl alcohol are poured on 1 part of red phosphorus in a well-cooled retort with reversed condenser, and 6 parts of bromine are gradually added. After two or three

* It will be remembered that the unsaturated hydrocarbon will also combine directly with halogen-hydrides to form substituted saturated hydrocarbons. It is to be noted that when this is the case the halogen attaches itself to the carbon atom which has the smallest number of hydrogen atoms attached to it. Thus, from propylene, $CH_3{\cdot}CH:CH_2$, and HCl, there results $CH_3{\cdot}CHCl{\cdot}CH_3$, isopropyl chloride, not $CH_3{\cdot}CH_2{\cdot}CH_2Cl$.

hours, heat is applied by a water-bath, and the vapour condensed by a freezing-mixture. Methyl bromide boils at 4°.5, burns feebly, and smells like chloroform.

Ethyl bromide, C_2H_5Br, may be prepared like methyl bromide, using 16 parts of absolute alcohol, 4 parts of red phosphorus, and 10 parts of bromine. It is a liquid boiling at 39° C.; sp. gr. 1.419.

Methyl iodide, CH_3I, is prepared on the same principle as the bromide. 10 parts of iodine being dissolved in 4 parts of methyl alcohol, and 1 part of red phosphorus added in small portions. After heating in a water-bath for some time, the mixture is distilled. The methyl iodide is the lower layer of the distillate. It has a pleasant smell, sp. gr. 2.29, and boils at 44° C. It mixes with alcohol, but not with water. When kept, it becomes brown from separation of iodine. It is converted into CH_3Cl gas when heated with $HgCl_2$ dissolved in ether. Hydriodic acid, at 150° C., converts it into CH_4. Methyl iodide is used in making aniline dyes.

Methyl fluoride, CH_3F, is a combustible gas obtained by heating KF with potassium methyl sulphate, KCH_3SO_4. *Ethyl fluoride* boils at −48° C.

Ethyl iodide, C_2H_5I, is prepared by pouring 5 parts of absolute alcohol on one part of red phosphorus in a retort, adding gradually 10 parts of iodine in powder, setting aside for twelve hours, and distilling in a water-bath with a good condenser. Ethyl iodide mixed with alcohol distils over, leaving phosphoric acid in the retort (together with some phosphethylic acid formed by its action on some of the alcohol), $3C_2H_5OH + P + I_3 = 3C_2H_5I + P(OH)_3$. The distillate is shaken, in a stoppered bottle, with about an equal measure of water and enough soda to render it alkaline. The ethyl iodide collects as an oily layer at the bottom; this is separated from the upper layer by a tap-funnel or pipette or siphon, allowed to stand with a little fused calcium chloride in coarse powder, to remove the water, and distilled.

Ethyl iodide has a pleasant smell, sp. gr. 1.93, and boiling-point 72° C. It becomes brown when kept, especially in the light, iodine being liberated, and butane formed; $2C_2H_5I = C_4H_{10} + I_2$. Ethyl iodide is sparingly dissolved by water, but readily by alcohol and ether.

Ethyl iodide is a very important reagent in organic researches for introducing the group C_2H_5 into the places of other radicles.

The monohalogen substitution-derivatives of the paraffins higher in the series than ethane, exist in isomeric forms exactly analogous to the isomeric alcohols (p. 567), a halogen being substituted for OH.

411. *Dihalogen derivatives of ethane* can obviously exist in two modifications, $CH_2X{\cdot}CH_2X$, or ethylene halides, and $CH_3{\cdot}CHX_2$, ethylidene halides. The former are obtained by the direct addition of halogen to ethylene, and since by judicious treatment with moist silver oxide they can be converted into glycol halogen-hydrins (*e.g.*, glycol chlor-hydrin, *q.v.*) they most probably have the formula assigned to them above; moreover, they may be prepared from the glycols by distillation with phosphorus halides. The ethylidene halides can be obtained from aldehyde by treatment with phosphorus pentahalides (p. 579).

Ethylene chloride, *ethene dichloride*, or *Dutch liquid*, $C_2H_4Cl_2$, may be obtained from glycol by distilling it with PCl_5—

$$C_2H_4(OH)_2 + 2PCl_5 = C_2H_4Cl_2 + 2POCl_3 + 2HCl;$$

but it is generally prepared by allowing equal volumes of dry ethene gas and dry chlorine to pass into a large inverted globe or flask, the neck of which passes through a cork into a receiver for the condensed liquid. Ethene dichloride smells rather like chloroform; its sp. gr. is 1.28, and it boils at 84° C.; it is nearly insoluble in water, but dissolves in alcohol.

Ethylidene chloride, CH_3CH_2Cl, is best prepared by the action of $COCl_2$ on $CH_3{\cdot}CHO$, carbon dioxide being liberated. B.-p. 60° C.

Ethylene bromide, or *ethene dibromide*, $C_2H_4Br_2$, is prepared as described at p. 574. It resembles the dichloride, but its sp. gr. is 2.16, and it boils at 131° C.

Ethylene iodide, $C_2H_4I_2$, obtained by heating iodine in olefiant gas, forms silky needles, which may be sublimed in the gas, but are easily decomposed into C_2H_4 and I_2.

The difference in the stability of ethene chloride, bromide, and iodide is shown by the action of alcoholic solution of potash, which converts ethene dichloride into *monochlorethene*, or *vinyl chloride*, $C_2H_4Cl_2 + KOH = C_2H_3Cl + KCl + H_2O$; whilst the dibromide yields, in addition to the vinyl bromide, a quantity of acetylene; $C_2H_4Br_2 + 2KOH = C_2H_2 + 2KBr + H_2O$; and the di-iodide is much more easily decomposed, giving very little vinyl iodide and much acetylene.

Methylene iodide, CH_2I_2, may be obtained by heating iodoform with strong HI in a sealed tube, at about 130° C., for some hours; $CHI_3 + HI = CH_2I_2 + I_2$. It is a liquid remarkable for its high specific gravity, 3.328, and is used for determining the specific gravities of precious stones. It boils at 181° C.

412. **Chloroform, or *tri-chloromethane*, $CHCl_3$, the anæsthetic, is prepared by distilling 1 part of alcohol (sp. gr. 0.834) with 10 parts of chloride of lime and 40 parts of water, at 65° C., until about 1½ part has passed over; the distilled liquid, consisting chiefly of water and chloroform, separates into two layers; the chloroform which is at the bottom, is drawn off, shaken with strong sulphuric acid to remove some impurities, and when it has risen to the surface it is separated and purified by distillation until it boils regularly at 61° C. (142° F.). Chloroform is prepared from acetone in a similar manner.**

The action of chloride of lime on alcohol has not been clearly explained; it might be expected that chloral would be formed at first by the oxidising and chlorinating actions, and that this would be converted into chloroform and calcium formate by the strongly alkaline calcium hydroxide in the chloride of lime (see *Chloral*), but much CO_2 is given off, causing frothing during the distillation. Probably the chloroform is produced by some such reaction as the following: $3C_2H_6O + 8Ca(OCl)_2 = 2CHCl_3 + 8H_2O + CO_2 + 5CaCl_2 + 3CaCO_3$. Pure chloroform is more easily prepared by decomposing chloral hydrate with potash or soda.

Chloroform is a very fragrant liquid of sp. gr. 1.50, and boiling-point 61°·5 C. It is very useful in the laboratory as a solvent, and is much used for extracting strychnine and other alkaloids from aqueous solutions. It is also one of the best solvents for caoutchouc. Chloroform is very slightly soluble in water, and gives it a sweet taste. Alcohol dissolves it in all proportions, and it is nearly as soluble in ether. Strong sulphuric acid does not affect it, and it is not coloured by pure chloroform. Aqueous solution of potash does not decompose it, but the alcoholic solution converts it into potassium chloride and potassium formate; $CHCl_3 + 4KOH = 3KCl + HCO{\cdot}OK + 2HOH$. If Dutch liquid ($C_2H_4Cl_2$) be present as an impurity in the chloroform, gaseous chlorethylene (C_2H_3Cl) is evolved. When heated with alcoholic potash and aniline, it yields phenyl-carbamine (*q.v.*), the powerful odour of which renders this a delicate test for chloroform.

Heated with alcoholic solution of ammonia in a sealed tube at 180° C., chloroform gives ammonium chloride and cyanide; $CHCl_3 + 5NH_3 = 3NH_4Cl + NH_4{\cdot}CN$. When potash is present a similar reaction occurs at the ordinary temperature, $CHCl_3 + NH_3 + 4KOH = KCN + 3KCl + 4H_2O$. Heated with potassium-amalgam, chloroform evolves acetylene: $2CHCl_3 + 3K_2 = C_2H_2 + 6KCl$. That chloroform is really a substitution-derivative from methane is shown by its conversion into that gas when dissolved in alcohol and heated with zinc-dust; by the formation of tetrachloro-methane, CCl_4, by the action of chlorine (in presence of iodine) upon

chloroform, and by that of dichloro-methane, CH_2Cl_2, by the action of zinc and sulphuric acid.

When chloroform is heated with sodium ethoxide, it is converted into *ortho-formic ether*; $CHCl_3 + 3NaOC_2H_5 = 3NaCl + CH(OC_2H_5)_3$.

Iodoform, CHI_3, or *tri-iodo-methane*, is a product of the action of iodine upon alcohol in an alkaline solution, the immediate agent being probably a hypo-iodite, whilst chloroform is produced by a hypo-chlorite. To prepare it, dissolve 32 parts of potassium carbonate in 80 parts of water, add 16 parts of alcohol of 95 per cent. and 32 parts of iodine; heat gently till the colour of the iodine has disappeared, when iodoform will be deposited on cooling.

$$CH_3{\cdot}CH_2OH + 6KOH + I_8 = CHI_3 + HCOOK + 5KI + H_2O.$$

To recover the iodine left as KI, the filtrate from the iodoform is mixed with 20 parts of HCl and 2.5 parts of potassium dichromate, which liberates the iodine. The liquid is neutralised with potassium carbonate, and 32 parts more of that salt are added, together with 6 parts of iodine and 16 of alcohol; the operations of heating and cooling are then repeated.

Iodoform is deposited in yellow shining hexagonal plates, smelling of saffron. It fuses at 120° C., and may be sublimed with slight decomposition. It is insoluble in water, but dissolves in alcohol and ether. When boiled with potash, it is partly volatilised with the steam, and partly decomposed, yielding potassium iodide and formate. The production of CHI_3 on adding iodine and dilute KOH and stirring, is a very delicate test for alcohol, but many other substances also yield it. Iodoform is used in medicine and surgery.

Bromoform, $CHBr_3$, is produced when bromine is added to an alcoholic solution of potash. It has a general resemblance to chloroform, but boils at 151° C. Crude bromine sometimes contains bromoform.

Chloriodoform, $CHICl_2$, is obtained by distilling iodoform with $HgCl_2$. It is a yellow liquid, b.-p. 131° C. The corresponding Br compound has been prepared.

Trichloropropane exists in several forms. The commonest of these is *glyceryl trichloride* or *trichlorhydrin*, $CH_2Cl{\cdot}CHCl{\cdot}CH_2Cl$; it is obtained by the action of PCl_5 upon glycerine, $C_3H_5(OH)_3 + 3PCl_5 = C_3H_5Cl_3 + 3HCl + 3POCl_3$. It is a liquid of pleasant smell, sp. gr. 1.42, and boiling at 158° C. It is sparingly soluble in water. *Tribromhydrin*, $C_3H_5Br_3$, is a crystalline solid; m.-p. 17° C.; b.-p. 220° C. The iodine compound corresponding with this does not appear capable of existing.

413. *Allyl chloride*, $CH_2 : CH{\cdot}CH_2Cl$, is obtained by distilling allyl alcohol with PCl_5. It has a pungent smell, sp. gr. 0.95, and boiling-point 46° C.; it is insoluble in water. *Allyl bromide* may be prepared by distilling allyl alcohol with KBr and H_2SO_4, mixed with an equal bulk of water. It is capable of combining with bromine to form *glyceryl* or *allyl tribromide*, $C_3H_5Br_3$, and with HBr to form $CH_2Br{\cdot}CH_2{\cdot}CH_2Br$, *trimethylene bromide*. *Allyl iodide*, C_3H_5I, is prepared from glycerine (200 parts) by adding iodine (135), filling the retort with CO_2 and adding, very gradually, vitreous phosphorus (40). The distilled liquid is washed with a little NaOH, and dried with $CaCl_2$. Probably, glyceryl tri-iodide is first produced: $C_3H_5(OH)_3 + P + I_3 = C_3H_5I_3 + P(OH)_3$; the tri-iodide is then decomposed into C_3H_5I and I_2. Allyl iodide has a very pungent odour of leeks, sp. gr. 1.8, and boiling-point 101° C. It is remarkable for combining with mercury, shaken with its alcoholic solution, to form *mercury allyl iodide*, $Hg''C_3H_5I$, deposited in colourless crystals, which become yellow in light, and yield HgI_2 and C_3H_5I when treated with iodine. Ag_2O, in presence of H_2O, substitutes OH for the I, producing $HgC_3H_5{\cdot}OH$, *mercury allyl hydroxide*, an alkaline base. Bromine converts allyl iodide into tribromhydrin, $C_3H_5Br_3$.

The *halogen propylenes*—*e.g.*, *α-chloropropylene*, $CH_3{\cdot}CH : CHCl$,—isomeric with the allyl halides, exist in a maleinoid and a fumaroid modification (p. 616).

Propargyl chloride, $CH \vdots C \cdot CH_2Cl$, is obtained by acting on propargyl alcohol with phosphorus chloride; it boils at 65° C.

414. (B) **Halogen derivatives of closed-chain hydrocarbons.**—These may be halogen substitution or addition products. The substitution may be either in the benzene or other nucleus, or in side-chains, or in both. Thus, while only 1 compound of the formula C_6H_5X exists, there are 4 of the formula C_7H_7X, namely, $C_6H_4X \cdot CH_3(3)$ and $C_6H_5 \cdot CH_2X$. Again, 3 compounds of the form $C_6H_4X_2$ are known, and 10 of the form $C_7H_6X_2$, viz., $C_6H_3X_2 \cdot CH_3(6)$, $C_6H_4X \cdot CH_2X(3)$ and $C_6H_5 \cdot CHX_2$.

The nucleal substitution-products are more stable than are the open-chain hydrocarbon substitution-products. Thus, C_6H_5Cl will not yield C_6H_5OH when treated with AgOH, whilst C_2H_5Cl yields C_2H_5OH by this treatment. But the side-chain substitution-products behave as open-chain derivatives.

The direct action of halogens on benzene itself produces chiefly substitution-products. In the case of its homologues, nucleal substitution occurs if the action be allowed to proceed in the cold, especially in the dark and in presence of iodine; whilst at higher temperatures, and in sunlight, side-chain substitution occurs. Thus, $C_6H_4Br \cdot CH_3$ is formed when Br attacks cold toluene, but $C_6H_5 \cdot CH_2Br$ if the temperature is higher.

The treatment of phenols (or alcohols) with phosphorus halides, and a special reaction to be described under *Diazo-compounds*, also yield these halogen derivatives.

Chlorobenzene or *phenyl chloride*, C_6H_5Cl, may be prepared by passing Cl into C_6H_6, containing 3 per cent. of Al_2Cl_6, until the calculated gain of weight is observed; or by the action of PCl_5 on phenol; $C_6H_5OH + PCl_5 = C_6H_5Cl + POCl_3 + HCl$; it is a colourless liquid, boiling at 132° C. *Bromobenzene* (b.-p. 155° C.) is similarly prepared. *Iodobenzene* (b.-p. 188° C.) may be obtained by heating benzene with iodine and HIO_3 (to absorb HI; p. 632) at 200° C. By dissolving it in $CHCl_3$ and passing Cl through the solution the *dichloride*, $C_6H_5I : Cl_2$ is prepared; this is of theoretical importance, since the iodine in it is trivalent; when it is treated with NaOH it yields *iodosobenzene*, $C_6H_5I : O$, which is a base forming salts such as $C_6H_5I : OCrO_3$; when heated it becomes iodobenzene and *iodoxybenzene*, $C_6H_5IO_2$, an explosive substance presumably containing pentavalent iodine.

o-and-*p*-*Chlorotoluenes*, $C_6H_4Cl \cdot CH_3$, are obtained by passing Cl into cold toluene containing iodine.

Benzyl chloride, $C_6H_5 \cdot CH_2Cl$ (b.-p. 176° C.), *benzal* (*benzylidene*) *chloride*, $C_6H_5 \cdot CHCl_2$ (b.-p. 213° C.), and *benzotrichloride*, $C_6H_5 \cdot CCl_3$ (b.-p. 213° C.), are obtained by chlorinating boiling toluene, the Cl being passed into the liquid until the increase of weight calculated for the particular compound required, has been attained. They are colourless liquids * and can be prepared by the action of PCl_5 on the corresponding oxygen compounds—viz., benzyl alcohol, benzoic aldehyde, and benzoic acid—into which they are converted by hydrolysis. They are intermediate products in the manufacture of benzaldehyde from toluene (p. 584).

Two of each of the *monohalogen substitution products of naphthalene* exist (p. 552). *α-Chloro-naphthalene*, $C_{10}H_7Cl$, is a colourless liquid (b.-p. 263° C.) and is the product of passing Cl into boiling naphthalene. *β-Chloro-naphthalene* crystallises in laminæ (m.-p. 61° C.; b.-p. 257° C.), and is obtained by treating β-naphthol, $C_{10}H_7 \cdot OH$, with PCl_5. Ten dichloro-naphthalenes are known. When naphthalene is chlorinated in the cold, the addition-product, *naphthalene tetrachloride*, $C_{10}H_8Cl_4$, is formed; this crystallises in colourless rhombohedra, melts at 182° C., and becomes $C_{10}H_6Cl_2$ when boiled with KOH. Since it yields phthalic acid and not a chlorophthalic acid when oxidised, all the Cl atoms must be in the same benzene nucleus, and the compound must have the orientation 1 : 2 : 3 : 4 (p. 552).

Anthracene dichloride, $C_6H_4 : (CHCl)_2 : C_6H_4$, is formed when chlorine is passed

* Benzyl chloride and benzyl bromide have a tear-exciting odour.

over cold anthracene, whilst at a high temperature *γ-chloranthracene* (m.-p. 103° C.) and *γ-dichloranthracene* (m.-p. 209° C.) are produced (p. 554) as yellow needles.

The halogen derivatives from other condensed benzene nuclei are of little importance.

415. **Halogen Compounds from Aldehydes and Acids.** — **Chloral** or *tri-chloraldehyde*, $CCl_3 \cdot CHO$, prepared by passing thoroughly dried chlorine into absolute alcohol, which must be placed in a vessel surrounded by cold water at first, because the absorption of chlorine is attended by great evolution of heat. The passage of chlorine is continued for many hours, and when the absorption is slow, the alcohol is gradually heated to boiling, the chlorine being still passed in until the liquid refuses to absorb it. The principal reaction is represented by the equation, $CH_3 \cdot CH_2 \cdot OH + 4Cl_2 = 5HCl + CCl_3 \cdot CHO$; but the HCl attacks part of the alcohol, forming ethyl chloride and water. On cooling, the product solidifies to a crystalline mixture of the compounds of water and alcohol with chloral, from which the latter may be obtained by distillation with sulphuric acid.

On the large scale, chlorine is passed into alcohol of at least 96 per cent. for 12 or 14 days. The crude product is heated with an equal weight of strong H_2SO_4, in a copper vessel lined with lead. HCl escapes at first, and the chloral distils over at about 100° C. The distillate is rectified, and mixed with water in glass flasks, when *chloral hydrate*, $CCl_3 \cdot CHO.H_2O$, is formed, which is poured into porcelain basins, where it crystallises.

Chloral is a liquid of sp. gr. 1.5, and boiling-point 97° C. It has a pungent, tear-exciting odour, and irritates the skin. Exposed to air, it absorbs water and forms crystals of the hydrate, which is produced at once when choral is stirred with a few drops of water, heat being evolved. When quite pure it may be kept unchanged, but, in presence of impurities, especially of sulphuric acid, it soon becomes an opaque white mass of *metachloral*, which is insoluble in water, alcohol, and ether. This is probably formed by the condensation of three molecules of chloral, into which it is reconverted at 180° C. It will be remembered that aldehyde is liable to a similar polymerisation. Chloral also resembles aldehyde in forming crystalline compounds with $NaHSO_3$, and in giving a mirror of silver with silver ammonio-nitrate. With ammonia it forms $CCl_3 \cdot CH(NH_2)(OH)$, corresponding with aldehyde-ammonia. Zinc and HCl substitute H_3 for the Cl_3 in chloral, converting it into aldehyde. Nitric acid oxidises it to *trichloracetic acid*, $CCl_3 \cdot CO_2H$, which forms deliquescent crystals and boils at 195° C. When heated with KCN and H_2O it yields *dichloracetic acid* (b.-p. 191° C.),

$$CCl_3 \cdot CHO + KCN + H_2O = CHCl_2 \cdot CO_2H + KCl + HCN.$$

Potash decomposes it easily; $CCl_3 \cdot CHO + KOH = CCl_3H + H \cdot CO \cdot OK$. Chloral is formed when starch or sugar is distilled with HCl and MnO_2.

Chloral hydrate, $CCl_3 \cdot CH(OH)_2$, *trichlorethylideneglycol*, forms prismatic crystals, which are very soluble in water and alcohol, and have the odour of chloral. It fuses at 57° C., and boils at 97°, but is dissociated into chloral and steam, which recombine on cooling. It is employed medicinally for procuring sleep.

Chloral alcoholate, $CCl_3 \cdot CH(OH)(OC_2H_5)$, formed when choral is dissolved in alcohol, crystallises like the hydrate, but is rather less soluble in water.

Bromal, obtained by action of Br on alcohol, is very similar to chloral.

Croton-chloral, or *butyl chloral*, $CH_3 \cdot CHCl \cdot CCl_2 \cdot CHO$, is ***α-α-β-trichlorobutyric aldehyde***, and is prepared by substituting aldehyde for alcohol in the preparation

of chloral, when croton-aldehyde is first produced, and is converted into butyl chloral; (1) $2CH_3CHO = CH_3{\cdot}CH : CH{\cdot}CHO + H_2O$; (2) $CH_3{\cdot}CH : CH{\cdot}CHO + 2Cl_2 = C_3H_4Cl_2{\cdot}CHO + HCl$. It is an oily liquid of pungent odour, sp. gr. 1.4, and boiling-point 164° C. It combines with water to form a hydrate which dissolves in hot water, and crystallises, on cooling, in plates which have a very irritating odour. It has been used in medicine.

416. **Halogen compounds from acids by substitution of halogen for hydroxyl**—*Acidyl halides.*—These bodies have their counterparts among inorganic compounds; thus, nitrosyl chloride, NOCl, is obtained by substituting Cl for OH in nitrous acid, NO·OH; and, in acetic acid, $CH_3{\cdot}CO{\cdot}OH$, a similar exchange gives acetyl chloride, $CH_3{\cdot}CO{\cdot}Cl$. Thus they are *haloidanhydrides* (p. 191), or the halides of negative radicles, just as the alkyl halides may be regarded as halides of positive radicles and compared with KCl.

They are generally prepared by the action of phosphorus halides on the acids.

No compound of this kind has been obtained from formic acid.

417. **Acetyl chloride,** $CH_3{\cdot}CO{\cdot}Cl$, or *acetic chloride*, is prepared by distilling acetic acid with phosphorus trichloride; $3CH_3COOH + PCl_3 = 3CH_3{\cdot}COCl + P_2O_3 + 3HCl$. To 5 parts by weight of glacial acetic acid, kept cool, are gradually added 4 parts of phosphorus trichloride, and the mixture distilled on a water-bath. The distillate may be rectified over fused sodium acetate to remove any phosphorus trichloride. The pentachloride may also be used,

$$CH_3{\cdot}COOH + PCl_5 = CH_3{\cdot}CO{\cdot}Cl + POCl_3 + HCl.$$

Acetyl chloride is a colourless liquid, which fumes in air, and has an irritating odour; its sp. gr. is 1.11, and it boils at 55° C. Water decomposes it with violence, yielding hydrochloric and acetic acids; $CH_3{\cdot}CO{\cdot}Cl + HOH = CH_3{\cdot}CO{\cdot}OH + HCl$. If alcohol be employed instead of water, ethyl acetate is produced; $CH_3{\cdot}CO{\cdot}Cl + C_2H_5{\cdot}OH = CH_3{\cdot}CO{\cdot}OC_2H_5 + HCl$. This mode of reaction renders *acetyl chloride a most useful reagent for discovering the constitution of alcohols.*

Some other instructive reactions produce acetyl chloride, such as that between acetic anhydride (di-acetyl oxide) and phosphorus pentachloride $(C_2H_3O)_2O + PCl_5 = 2C_2H_3OCl + POCl_3$; or between phosphorus oxychloride and sodium acetate—$POCl_3 + 2CH_3COONa = 2CH_3COCl + NaPO_3 + NaCl$; it was thus that acetyl chloride was first made. By distilling sodium acetate with acetyl chloride, acetic anhydride is obtained—$C_2H_3O{\cdot}ONa + C_2H_3O{\cdot}Cl = (C_2H_3O)_2O + NaCl$. By careful treatment with sodium-amalgam and snow, ethyl alcohol has been prepared from acetyl chloride: $C_2H_3OCl + H_4 = C_2H_5OH + HCl$.

Acetyl bromide, $CH_3{\cdot}CO{\cdot}Br$, is prepared by distilling acetic acid with bromine and phosphorus; it resembles the chloride, but boils at 81° C., and becomes yellow when kept. *Acetyl iodide*, $CH_3{\cdot}CO{\cdot}I$, is less stable, and is prepared by distilling acetic anhydride with iodine; it boils at 108° C.

Benzoyl chloride, or *benzoic chloride*, $C_6H_5{\cdot}CO{\cdot}Cl$, is prepared by distilling benzoic acid with PCl_5. It is a pungent smelling liquid, of sp. gr. 1.11, and boiling-point 199° C. It is decomposed by water, but more slowly than is acetyl chloride, yielding benzoic, and hydrochloric acids. It may also be obtained by the action of chlorine on bitter-almond oil (benzoic aldehyde); $C_6H_5{\cdot}CO{\cdot}H + Cl_2 = C_6H_5{\cdot}CO{\cdot}Cl + HCl$.

When hydroxy-acids are distilled with PCl_5, the alcoholic OH groups are also exchanged for Cl. Thus lactic acid yields *α-chloropropionic chloride* (*lactyl chloride*), $CH_3{\cdot}CHCl{\cdot}COCl$. Salicylic acid yields *1 : 2-chlorobenzoic chloride* (*salicylic chloride*). With water these chlorides yield HCl and the corresponding chloro-acid.

Succinyl dichloride, $C_2H_4(COCl)_2$, is obtained by distilling succinic acid with

PCl_5; $C_2H_4(CO\cdot OH)_2 + 2PCl_5 = C_2H_4(COCl)_2 + 2POCl_3 + 2HCl$. It is a fuming liquid, of sp. gr. 1·39, boiling at 190° C. With water it yields HCl and succinic acid, but it is doubtful whether it is a true acid chloride, or resembles phthalyl chloride (*v.i.*).

Fumaryl dichloride, $C_2H_2(CO\cdot Cl)_2$, is the product of the distillation of fumaric acid, $C_2H_2(CO\cdot OH)_2$, and of its isomeride, maleic acid, with phosphoric chloride. It boils at 160° C. Malic acid also yields fumaryl dichloride when distilled with PCl_5; $C_2H_3(OH)(CO\cdot OH)_2 + 3PCl_5 = C_2H_2(CO\cdot Cl)_2 + 3POCl_3 + 4HCl$.

Tartaric acid, $C_2H_2(OH)_2(COOH)_2$, heated with phosphoric chloride, is converted into *chloromaleic chloride*, $C_2HCl(CO\cdot Cl)_2$, an oily liquid which yields crystals of *chloromaleic acid*, $C_2HCl(CO\cdot OH)_2$, when decomposed by water.

Phthalyl dichloride is obtained by distilling phthalic acid, $C_6H_4(CO\cdot OH)_2$, with PCl_5. It is a yellow, oily liquid, boiling at about 275° C. It is more stable than most other compounds of this class, being slowly decomposed by water into HCl and phthalic acid. Even solution of NaOH only slowly decomposes it. It appears to have the constitution $C_6H_4\begin{cases}CCl_2\\CO\end{cases}O$, not $C_6H_4\begin{cases}COCl\\COCl\end{cases}$, since nascent H converts it into *phthalide*, $C_6H_4\begin{cases}CH_2\\CO\end{cases}O$, a lactone from 1 : 2-*hydroxymethylbenzoic acid*, $CH_2OH\cdot C_6H_4\cdot COOH$.

VII. ETHEREAL SALTS OR ESTERS.

418. These compounds, formed by the substitution of a hydrocarbon radicle for the hydroxylic hydrogen in an acid, are numerous and important. They correspond in composition with the salts formed from acids by substitution of metals for basic hydrogen. For example:

Potassium sulphate, $SO_2\begin{cases}OK\\OK\end{cases}$; methyl sulphate, $SO_2\begin{cases}OCH_3\\OCH_3\end{cases}$.

Potassium hydrogen sulphate, $SO_2\begin{cases}OK\\OH\end{cases}$; methyl hydrogen sulphate, $SO_2\begin{cases}OCH_3\\OH\end{cases}$.

Potassium acetate, $CH_3\cdot COOK$; methyl acetate, $CH_3\cdot COOCH_3$.

It will be seen that the ethereal salts of the organic acids consist of an acidyl group and a hydrocarbon radicle united by an oxygen atom, thus resembling the ethers; hence the name *esters*, or *compound ethers*.

They may be formed (*a*) by heating an alcohol with an acid, whereby water is eliminated:

(1) $CH_3\cdot OH + NO_2\cdot OH \rightleftarrows NO_2\cdot OCH_3 + HOH$.

(2) $CH_3OH + SO_2(OH)_2 \rightleftarrows SO_2(OH)(OCH_3) + HOH$.

(3) $CH_3OH + CH_3COOH \rightleftarrows CH_3\cdot COOCH_3 + HOH$.

These reactions are reversible and consequently never complete. With polybasic acids the hydrogen salts are generally obtained.

(*b*) By heating a chloranhydride with an alcohol:

(4) $CH_3OH + CH_3\cdot COCl = CH_3\cdot COOCH_3 + HCl$;

(*c*) by heating a halogen derivative of a hydrocarbon with the silver salt of an acid:

(5) $2CH_3I + Ag_2SO_4 = (CH_3)_2SO_4 + 2AgI$.

The ethereal salts exhibit a resemblance to the metallic salts in being decomposed by the hydroxides of the alkali-metals, with formation of the alcohol corresponding with the radicle of the ethereal salt, and of a salt of the alkali-metal; thus, ethyl acetate, heated with potash,

yields ethyl alcohol and potassium acetate; $CH_3{\cdot}CO_2C_2H_5 + KOH = C_2H_5{\cdot}OH + CH_3{\cdot}CO_2K$. A reaction of this kind is termed the *saponification* of the ethereal salt, because the formation of soap is effected in a similar way by the action of alkalies on the fats and oils, which are ethereal salts formed by glycerine with the higher members of the acetic series of acids.

Many of the ethereal salts are volatile liquids, having characteristic, fruity odours.

When treated with NH_3 they yield an alcohol and an acid amide: $CH_3{\cdot}COOCH_3 + NH_3 = CH_3{\cdot}CONH_2 + CH_3OH$. Heated with water or dilute acids they are hydrolysed to the free acid and the alcohol: $CH_3{\cdot}COOCH_3 + HOH = CH_3{\cdot}COOH + CH_3{\cdot}OH$. With strong halogen acids they yield the free acid and the halide of the hydrocarbon radicle: $CH_3{\cdot}COOCH_3 + HCl = CH_3{\cdot}COOH + CH_3Cl$.

419. **Sulphuric Esters.**—*Methyl hydrogen sulphate* or *sulphomethylic acid*, CH_3HSO_4.—Methyl alcohol (1 weight) is slowly added to strong H_2SO_4 (2 weights), and the mixture is heated to boiling, cooled, and neutralised with $BaCO_3$, which precipitates the excess of H_2SO_4 as $BaSO_4$, leaving *barium sulphomethylate* in solution: this is evaporated on a steam-bath, and finally *in vacuo*, when square tables of $Ba(CH_3SO_4)_2.2Aq$. crystallise. By adding an equivalent of H_2SO_4 to a solution of these, the barium is precipitated and the solution of sulphomethylic acid may be concentrated in *vacuo* to a syrupy liquid. See equation 2 above. It is an unstable compound, decomposed at 130° C. into H_2SO_4 and methyl sulphate, $2CH_3HSO_4 = (CH_3)_2SO_4 + H_2SO_4$, and by boiling with water, into CH_3OH and H_2SO_4. Heated with an alcohol, it gives the corresponding mixed ether, $CH_3HSO_4 + R{\cdot}OH = CH_3{\cdot}O{\cdot}R + H_2SO_4$. The basic hydrogen in CH_3HSO_4 may be exchanged for a metal forming *sulphomethylates*, which are all soluble in water. The acid is also formed by gradually adding CH_3OH to well-cooled chlorosulphonic acid (a chloranhydride, *cf.* equation 4 above): $CH_3OH + SO_2(OH)Cl = HCl + CH_3HSO_4$.

Methyl sulphate, $(CH_3)_2SO_4$, is prepared by gradually adding CH_3OH (1 weight) to strong H_2SO_4 (8 weights) and distilling the mixture. The portion which distils at 150° C. is shaken with water, and the lower layer rectified over $CaCl_2$. Much of the CH_3 group is, however, broken up in this process. A better result is obtained by distilling sulphomethylic acid at 130° under diminished pressure. It is a liquid of peculiar odour, sp. gr. 1.32, and boiling-point 188° C. It does not dissolve in water, but is slowly decomposed, yielding methyl alcohol and sulphomethylic acid. Many of its reactions resemble those of inorganic salts; thus, if distilled with NaCl, it yields methyl chloride, CH_3Cl, and Na_2SO_4. With sodium formate it gives methyl formate and Na_2SO_4.

Sulphethylic or *ethyl-sulphuric* or *sulphovinic acid*, $HC_2H_5SO_4$, is prepared in the same way as sulphomethylic acid, employing equal weights of alcohol and sulphuric acid. It is a viscid liquid, very similar in its properties and reactions to sulphomethylic acid. The *sulphethylates* are soluble and easily crystallisable salts, prepared by adding the metallic carbonate to a solution made by heating alcohol with twice its weight of strong H_2SO_4, and, after cooling, diluting with water. The solution is then crystallised. The *calcium* salt is $Ca(C_2H_5SO_4)_2.2Aq$.

Sulphethylic acid is formed when ethylene is absorbed by H_2SO_4 (p. 535).

Ethyl sulphate, $(C_2H_5)_2SO_4$, is obtained by the reaction between ethyl iodide and Ag_2SO_4 in a sealed tube at 150° C.; $2C_2H_5I + Ag_2SO_4 = 2AgI + (C_2H_5)_2SO_4$. It is a fragrant liquid, of sp. gr. 1.18, and boiling-point 208° C. It does not mix with water, and is scarcely decomposed by it in the cold, but when heated with it yields alcohol and sulphethylic acid. Heated alone, it is decomposed into ethene and sulphuric acid: $(C_2H_5)_2SO_4 = 2C_2H_4 + H_2SO_4$.

Ethyl sulphate may also be obtained by passing vapour of SO_3 into well-cooled ether: $SO_3 + (C_2H_5)_2O = (C_2H_5)_2SO_4$. It is obtained as a secondary product in the preparation of ether, forming the bulk of the liquid called *heavy oil of wine*.

Phenyl-sulphuric acid is unknown; *potassium phenylsulphate*, $SO_2{\cdot}OC_6H_5{\cdot}OK$, is obtained by the prolonged action of $KHSO_4$ on phenol dissolved in potash; $C_6H_5{\cdot}OK + 2SO_2OHOK = SO_2{\cdot}OC_6H_5{\cdot}OK + SO_2(OK)_2 + H_2O$. The product is extracted with hot alcohol, from which it crystallises in tables soluble in water. It

is decomposed by exposure to moist air, or by boiling with water or dilute HCl, yielding phenol and $KHSO_4$; $SO_2{\cdot}OC_6H_5{\cdot}OK + HOH = HO{\cdot}C_6H_5 + SO_2{\cdot}OH{\cdot}OK$.

420. **Nitric Esters.**—The type is *ethyl nitrate* or *nitric ether*, prepared, on a small scale only lest explosion occur, from C_2H_5OH and HNO_3, carefully purified from HNO_2. 80 grams of nitric acid of sp. gr. 1·4 are heated on a steam-bath, and about 2 grams of urea nitrate are added, the urea of which decomposes any nitrous acid, $2HNO_2 + CO(NH_2)_2 = CO_2 + N_4 + 3H_2O$. After a time the mixture is well cooled and 15 grams more urea nitrate are added, followed by 60 grams of alcohol of sp. gr. 0.81. By fractional distillation dilute alcohol is first obtained, and then a mixture of alcohol and nitric ether, from which the latter is separated by adding water containing a very little KOH: the lower layer is drawn off, dried with calcium chloride, and distilled, $C_2H_5OH + HNO_3 = C_2H_5{\cdot}NO_3 + HOH$. The nitrous acid is destoyed because it rapidly oxidises the alcohol to aldehyde and other products which react very violently with nitric acid.

Ethyl nitrate has a very pleasant smell, and sp. gr. 1.1: it boils at 86° C., and its vapour explodes when heated, from the sudden disengagement of H_2O and CO_2. Water dissolves it very sparingly. Alcoholic solution of potash converts it into KNO_3 and alcohol.

421. **Nitrous Esters.**—*Ethyl nitrite*, $C_2H_5NO_2$, is the chief product of the action of nitric acid upon alcohol, until it becomes very violent, the nitric radicle NO_3 being reduced to the nitrous radicle NO_2 by the conversion of part of the alcohol into aldehyde. To prepare pure ethyl nitrite, 100 c.c. of a solution containing 46 grams of potassium nitrite are mixed with 50 c.c. of alcohol, and the mixture allowed to run slowly into a cooled mixture of 50 c.c. of alcohol, 100 c.c. of water, and 75 grams of sulphuric acid. The ethyl nitrite is distilled over by the heat of reaction, and is condensed by ice. It is purified by shaking with a little dry potassium carbonate.

Ethyl nitrite is much lighter and more volatile than the nitrate, its sp. gr. being 0.95, and its boiling-point 16° C. It has a yellowish colour, and a pleasant odour of apples. Like many other nitrous and nitric ethereal salts, it may be preserved unchanged if perfectly pure, but if water or other impurities be present, it decomposes, becoming acid, evolving red vapours, and bursting the bottle. Alcoholic potash converts it into KNO_2 and alcohol.

The *spiritus ætheris nitrosi*, or *sweet spirit of nitre*, used in medicine, is made by carefully adding 2 measured ounces of sulphuric acid to a pint of rectified spirit, slowly adding 2½ measured ounces of nitric acid to the cooled mixture, pouring it upon 2 ounces of fine copper wire in a retort with a good condenser, and distilling between 77° C. and 80°, until 12 measured ounces have distilled. Half an ounce more nitric acid is then poured into the retort, and three more ounces distilled over; the distillate is then mixed with two pints of rectified spirit. Hence the sweet spirit of nitre consists chiefly of spirit of wine, holding in solution ethyl nitrite, aldehyde, and some other products of the reaction. The proportion of ethyl nitrite present varies greatly, according to the efficiency of the condenser. Less is found in old samples, in consequence of volatilisation and chemical change. The presence of aldehyde is shown by the brown colour (aldehyde-resin) which it gives when shaken with alcoholic potash. Neglecting secondary changes, the formation of the ethyl nitrite in the above process may be represented by $C_2H_5{\cdot}OH + HNO_3 + H_2SO_4 + Cu = C_2H_5NO_2 + CuSO_4 + 2H_2O$.

It will be noticed that the alkyl nitrites are isomeric with the *nitro-paraffins*.

Amyl nitrite, $C_5H_{11}NO_2$, may be prepared by distilling amyl alcohol with potassium nitrite and sulphuric acid, or by passing N_2O_3 into amyl alcohol; it is a yellow liquid of sp. gr. 0.9, and boiling-point 96° C. It has a remarkable smell, and the peculiar effect of its vapour when inhaled has led to its employment in medicine. The vapour of amyl nitrite explodes when heated.

422. **Esters from polybasic acids** are mainly of theoretical importance, helping to settle the number of OH groups in the acid. They are generally obtained by the action of organic acids on the chloranhydrides, such as $POCl_3$, PCl_3, $AsCl_3$, BCl_3, $SiCl_4$, &c. Three *ethyl phosphates*, $PO(C_2H_5)_3$, $PO(OH)(C_2H_5)_2$ and $PO(OH)_2(OC_2H_5)$ and an *ethyl metaphosphate*, $P(OC_2H_5)_3$ are known. So also *ethyl arsenite* $As(OC_2H_5)_3$, b.-p. 166° C.; *ethyl borate* or *boric ether*, $B(OC_2H_5)_3$, b.-p. 119° C., which burns with a green flame; and several ethyl *silicates* or *silicic ethers*, such as $Si(OC_2H_5)_4$ (b.-p. 165° C.), which burns with a bright flame emitting clouds of SiO_2, are known. Water decomposes them into alcohol and acid.

Particularly interesting is the formation of ethereal salts of acids which cannot

exist in the free state. Thus *ethyl carbonate*, $CO(OC_2H_5)_2$, b.-p. 126° C., is obtained by heating silver carbonate with ethyl iodide in a sealed tube, although H_2CO_3 is unknown. *Potassium ethyl carbonate*, *potassium carbethylate* or *carbovinate*, $CO(OC_2H_5)(OK)$, is precipitated in crystals when CO_2 is passed into a cooled solution of KOH in absolute alcohol.

Again, *ethyl orthocarbonate*, $C(OC_2H_5)_4$, b.-p. 159° C., formed on the type of orthocarbonic acid $C(OH)_4$ (p. 261), is obtained when chloropicrin is treated with sodium ethoxide in alcohol, $CCl_3NO_2 + 4C_2H_5ONa = C(OC_2H_5)_4 + 3NaCl + NaNO_2$.

Xanthic acid, $CS(OC_2H_5)(SH)$, may be regarded as the acid ethyl salt of sulphothiocarbonic acid, $HO{\cdot}CS{\cdot}SH$,* which is not known in the free state. Xanthic acid is obtained as a potassium salt by saturating alcohol with KOH and stirring with excess of CS_2; $C_2H_5{\cdot}OH + CS_2 + KOH = HOH + CS(OC_2H_5)(SK)$. This salt forms colourless crystals with a faint odour, soluble in water and alcohol, but not in ether. When it is added to dilute HCl cooled in ice, xanthic acid separates as a heavy colourless oily liquid, which is decomposed at 24° C. into alcohol and CS_2. The characteristic reaction of the xanthates is that with cupric sulphate, which gives at first a dark-brown precipitate of *cupric xanthate*, rapidly decomposing into a yellow oil *xanthogen persulphide*, and bright yellow flakes of *cuprous xanthate*, the reaction being apparently—$2(C_2H_5O{\cdot}CS_2)_2Cu = (C_2H_5O{\cdot}CS_2)_2Cu_2 + 2(C_2H_5O{\cdot}CS_2)$.

From this reaction the acid was named (ξανθος, yellow).

423. **Formic Esters.**—*Methyl formate*, $HCOOCH_3$, is obtained by distilling sodium formate with KCH_3SO_4; $HCO_2Na + KCH_3SO_4 = HCO_2CH_3 + KNaSO_4$. It is isomeric with acetic acid, CH_3CO_2H, but boils at 32°·5 C. The whole of its hydrogen may be exchanged for chlorine, yielding $ClCO_2CCl_3$, *chloromethyl formate*, which is decomposed by heat into $2COCl_2$, carbonyl chloride.

Ethyl formate, or *formic ether*, $HCO_2C_2H_5$ (b.-p. 55° C.) is prepared by distilling sodium formate (7 weights) with H_2SO_4 (10) and alcohol (6). The distillate is freed from acid by shaking with a little lime, and redistilled. It is a fragrant liquid, used for flavouring rum. It dissolves in nine times its weight of water. Formic ether is also prepared by heating molecular proportions of alcohol and oxalic acid with glycerine for some time in a flask with a reversed condenser, and distilling (see p. 589).

424. **Acetic Esters.**—*Methyl acetate*, $CH_3CO_2CH_3$ (b.-p. 57° C.), prepared by distilling methyl alcohol with dried lead acetate and sulphuric acid, is a fragrant liquid, lighter than water, with which it mixes freely. It is a constituent of crude wood-spirit.

Ethyl acetate or *acetic ether*, $CH_3{\cdot}COOC_2H_5$.—Mix 50 c.c. of absolute alcohol with 50 c.c. of strong H_2SO_4 and heat to 140° C. in a flask with a good condenser. Run in through a tap funnel a mixture of 400 c.c. of alcohol and 400 c.c. of glacial acetic acid at the rate at which the ethyl acetate distils. Neutralise the distillate with Na_2CO_3, separate and shake the upper layer with equal weights of water and $CaCl_2$ to extract alcohol. Separate, dry the upper layer with $CaCl_2$, and distil.

Ethyl acetate boils at 77° C. and smells of cider; its sp. gr. is 0.91 and it dissolves in 11 times its weight of water, slowly decomposing into CH_3COOH and C_2H_5OH. It mixes readily with alcohol and ether, and is useful as a solvent and for flavouring. Chlorine converts it into *perchloracetic ether*, $CCl_3{\cdot}CO_2{\cdot}C_2Cl_5$, which smells of chloral.

425. **Ethyl aceto-acetate**, $CH_3CO{\cdot}CH_2CO_2C_2H_5$ (see aceto-acetic acid, p. 626), is prepared by acting on ethyl acetate with sodium, treating the product with a dilute acid, diluting with saturated brine and distilling the light oil which separates. It boils at 181° C. The simplest equation is—

$$2CH_3{\cdot}CO_2C_2H_5 + Na_2 = CH_3CO{\cdot}CHNaCO_2C_2H_5 + C_2H_5ONa + H_2.$$

The sodium in the *ethyl sodacetoacetate* being then exchanged for H by the dilute acid. But the change does not occur between *pure* ethyl acetate and Na; some alcohol must be present. It is supposed, therefore, that the first step is the direct addition of sodium ethoxide, C_2H_5ONa, to ethyl acetate producing the compound $CH_3C(OC_2H_5)_2(ONa)$. This is a derivative of the hypothetical *orthoacetic acid*, $CH_3C(OH)_3$, and with another molecule of ethyl acetate yields the ethyl sodacetoacetate and alcohol which reacts with more sodium to repeat the cycle.

Ethyl acetoacetate is a colourless liquid, smelling of hay. It is sparingly soluble

* In thio-acids, the S which is substituted for the carbonyl O is indicated by the prefix *sulpho-*, or *thiom-*, the prefix thio- being confined to the S that is substituted for the hydroxyl O.

in water, but dissolves in alcohol, the solution giving a violet colour with Fe_2Cl_6 and a green crystalline precipitate, $Cu(C_6H_9O_3)_2$, with a strong solution of copper acetate. It has an acid bias, for alkalies dissolve it and acids re-precipitate it from the solutions; but alkali carbonates will not dissolve it.

Ethyl acetoacetate is of great utility in synthetic chemistry, since through its means a variety of complex acids and ketones can be synthesised. This is rendered possible by two facts: (1) When ethyl acetoacetate is heated with alkalies it yields either a ketone (acetone) or an acid (acetic acid) according to the concentration of the alkaline solution. Thus, with *dilute* aqueous alcoholic potash the reaction is—

$$CH_3{\cdot}CO{\cdot}CH_2 \vdots CO_2C_2H_5 + 2KOH = CH_3{\cdot}CO{\cdot}CH_3 + K_2CO_3 + C_2H_5OH,$$

whilst with *concentrated* alcoholic potash the reaction is—

$$CH_3{\cdot}CO \vdots CH_2{\cdot}CO_2C_2H_5 + 2KOH = 2(CH_3{\cdot}CO_2K) + C_2H_5OH.$$

The first type of decomposition is called *ketonic decomposition*, the second is *acidic decomposition*. (2) Only one of the two methylene H atoms can be exchanged for sodium, but when ethyl sodacetoacetate is treated with an alkyl iodide, the sodium is exchanged for the alkyl group; thus, *ethyl ethylacetoacetate* may be prepared. $CH_3{\cdot}CO{\cdot}CHNa{\cdot}CO_2C_2H_5 + C_2H_5I = CH_3{\cdot}CO{\cdot}CHC_2H_5{\cdot}CO_2C_2H_5 + NaI$. By treating this with Na, *ethyl sodethylacetoacetate*, $CH_3{\cdot}CO{\cdot}CNaC_2H_5{\cdot}CO_2C_2H_5$, is formed, and with C_2H_5I this becomes *ethyl diethylacetoacetate* $CH_3{\cdot}CO{\cdot}C(C_2H_5)_2{\cdot}CO_2C_2H_5$. Other alkyl radicles may be substituted instead of ethyl. These substituted acetoacetates may be represented by the general formula $CH_3{\cdot}CO{\cdot}CRR'{\cdot}CO_2C_2H_5$, and such a compound yields the substituted ketone $CH_3{\cdot}CO{\cdot}CHRR'$ or the substituted acid $CHRR'{\cdot}CO_2H$ (together with acetic acid), accordingly as it is made to undergo the ketonic or the acidic decomposition described above.

Ethyl acetoacetate combines with phenylhydrazine and hydroxylamine like a ketone (p. 615), indicating a ketone group. By reduction it yields the secondary alcoholic-acid, $CH_3{\cdot}CHOH{\cdot}CH_2{\cdot}CO_2H$ (*β-hydroxybutyric acid*). It is a fact, however, that in many respects ethylacetoacetate behaves as though it were ethyl *β-hydroxyisocrotonate*, $CH_3{\cdot}COH : CH{\cdot}CO_2C_2H_5$. This is explained by supposing that it can exist both in this form and in that given above, under the influence of different reagents (*Tautomerism*. See *Cyanic Acid*).

When ethyl acetoacetate is heated it yields *dehydracetic acid*, $C_8H_8O_4$, (*6-methyl-3-acetopyranone*), which forms sparingly soluble, fusible crystals, unchanged by the strongest acids, but hydrolysed by alkalies, $C_8H_8O_4 + 3H_2O = CO_2 + CH_3{\cdot}CO{\cdot}CH_3$ (*acetone*) $+ 2(CH_3{\cdot}CO_2H)$.

Phenyl acetate, $C_6H_5{\cdot}C_2H_3O_2$ may be obtained by the reaction, $C_6H_5{\cdot}OH - C_2H_3O{\cdot}Cl = C_6H_5{\cdot}OC_2H_3O + HCl$, proving that phenol contains an OH group. It boils at 195° C. A piece of hard glass tube becomes invisible in phenyl acetate, its index of refraction for light being the same as that of the liquid.

One of the *amyl acetates*, $CH_3{\cdot}CO_2C_5H_{11}$, is sold as *pear essence*: and is prepared by distilling fusel oil with acetic and sulphuric acids; boils at 140° C.

426. **Esters of Higher Fatty Acids.**—*Ethyl butyrate*, or *butyric ether*, $C_3H_7{\cdot}CO_2C_2H_5$, prepared by distilling butyric acid with C_2H_5OH and H_2SO_4 is sold, dissolved in alcohol, as *ananas oil*, or *essence of pineapple*, which it resembles in odour. B.-p. 121° C.

Ethyl pelargonate, or *pelargonic ether*, $C_8H_{17}{\cdot}CO_2C_2H_5$, prepared from oil of rue, is used in flavouring as *quince oil*, and is present in the fruit.

Ethyl caprate, or *capric ether*, $C_9H_{19}{\cdot}CO_2C_2H_5$ (b.-p. 187° C.), was formerly called *œnanthic ether*, because it is found in old wine. It is made by distilling wine-lees, and, when pure, is a colourless, fragrant, oily liquid. It is sold for flavouring.

Amyl valerate, $C_4H_9{\cdot}CO_2C_5H_{11}$, or *apple oil*, is obtained by distilling fusel oil with sodium valerate and sulphuric acid; its boiling-point is 188° C.

The ethyl salts of acids of the acetic series containing more than ten atoms of carbon are generally prepared by dissolving the acids in alcohol and passing HCl into the solution; probably this converts the alcohol into C_2H_5Cl, which acts upon the acid to form the ethyl salt: this is deposited in crystals from the alcoholic solution. *Ethyl palmitate* and *stearate* are very fusible crystalline solids.

427. *Cetyl palmitate* (m.-p. 49° C.) and *ceryl cerotate* (m.-p. 81° C.) See p. 570.

Melissyl palmitate, or *myricin*, $C_{15}H_{31}{\cdot}CO_2C_{30}H_{61}$, forms about one-third of *bees'-*

wax, the colour, odour, and tenacity of which appear to be due to the presence of about 5 per cent. of a greasy substance called *cerolein*.

428. **Aromatic Esters.**—*Ethyl benzoate* or *benzoic ether*, $C_6H_5{\cdot}CO_2C_2H_5$, is prepared by dissolving benzoic acid in alcohol, saturating with HCl, distilling, and mixing the distillate with water, when ethyl benzoate separates as a fragrant liquid of sp. gr. 1.05, boiling at 213° C. *Benzyl benzoate*, $C_6H_5{\cdot}CO_2C_7H_7$, is a crystalline substance, contained in *balsam of Peru*; m.-p. 20° C.; b.-p. 323° C. *Benzyl cinnamate*, $C_8H_7{\cdot}CO_2C_7H_7$, (*cinnamein*), is present in the balsams of Peru and Tolu.

Methyl salicylate, $C_6H_4OH{\cdot}CO_2CH_3$, occurs in *oil of winter-green*, extracted from the flowers of *Gaultheria procumbens*, and was one of the first vegetable products prepared artificially. It is obtained by distilling methyl alcohol with sulphuric acid and salicylic acid. It is a fragrant liquid of sp. gr. 1.2, and boiling-point 224° C. Ferric chloride colours it violet. On treating it with strong solution of soda, in the cold, it yields crystals of $C_6H_4ONa{\cdot}CO_2CH_3$. When this is heated with methyl iodide in a sealed tube, it gives $C_6H_4OCH_3{\cdot}CO_2CH_3$, or *methyl methyl-salicylate*, an oily liquid. If this be saponified by potash, it yields the potassium salt of *methyl salicylic acid*, $C_6H_4OCH_3{\cdot}CO_2H$, a crystalline acid isomeric with methyl salicylate, but not giving the violet colour with ferric chloride. The *ethyl salicylate* resembles the methyl compound.

Phenyl salicylate, $C_6H_4OH{\cdot}CO_2C_6H_5$, is prepared by the action of $POCl_3$ on a mixture of salicylic acid and phenol, $2C_6H_4OH{\cdot}COOH + 2C_6H_5OH + POCl_3 = 2C_6H_4OH{\cdot}CO_2C_6H_5 + HPO_3 + 3HCl$; it crystallises in tables, melts at 43° C., and is used as an anti-pyretic under the name of *salol*.

Cinnamyl cinnamate, or *styracin*, $C_8H_7{\cdot}CO_2{\cdot}C_9H_9$, is a crystalline ethereal salt obtained from *storax* by treatment with soda.

429. **Esters from Dibasic Organic Acids.**—These may be acid or normal, both being generally obtained by distilling the anhydrous acid with an alcohol and fractionating the distillate.

Methyl oxalate, $(CO_2)_2(CH_3)_2$, (b.-p. 163° C.), obtained by distilling CH_3OH with an equal weight of H_2SO_4 and oxalic acid, solidifies in scales (m.-p. 51° C.) in the receiver; when distilled with water it is hydrolysed.

Ethyl oxalate, or *oxalic ether*, $(CO_2{\cdot}C_2H_5)_2$, is prepared by boiling equal weights of dried oxalic acid and absolute alcohol for six hours in a retort with a reversed condenser, and then adding water, which separates the oxalic ether as a fragrant liquid of sp. gr. 1.09, boiling at 186° C. It is hydrolysed by boiling with water, and saponified by potash. If mixed with one equivalent of potash, it yields pearly scales of potassium oxalethylate; $(CO_2{\cdot}C_2H_5)_2 + KOH = (CO_2)_2KC_2H_5 + C_2H_5{\cdot}OH$. By decomposing this with hydrofluosilicic acid, *oxalethylic* or *oxalovinic acid*, $(CO_2)_2HC_2H_5$, is obtained, but it is easily decomposed by water.

By the action of sodium on an ethereal solution of ethyl oxalate and acetate, the sodium derivative of *ethyl oxalacetate* is obtained; this has the formula $CO_2C_2H_5{\cdot}CO{\cdot}CH_2{\cdot}CO_2C_2H_5$, and, when heated with dilute H_2SO_4 yields *pyruric acid*, (p. 626).

Ethyl malonate, or *malonic ether*, $CH_2(CO_2{\cdot}C_2H_5)_2$, is prepared by passing HCl gas into absolute alcohol, containing calcium malonate in suspension—

$$CH_2(CO_2)_2Ca + 2(C_2H_5OH) + 2HCl = CH_2(CO_2{\cdot}C_2H_5)_2 + CaCl_2 + 2\,HOH.$$

After some hours' standing, the liquid is boiled on a steam-bath, again saturated with HCl gas, the alcohol distilled off, the liquid neutralised with sodium carbonate, and mixed with water, when the malonic ether separates as a bitter aromatic liquid of sp. gr. 1.068, and boiling-point 198° C. Its application for the preparation of fatty acids has been already noted (p. 587).

The ethereal salts of an alcohol radicle may be converted into those of another alcohol radicle by mixing them with the alcohol in question, and adding a small quantity of a metallic alkyl oxide, the action of which has not been fully explained. Thus, methyl oxalate dissolved in ethyl alcohol, and mixed, in the cold, with a small quantity of sodium ethoxide, $C_2H_5{\cdot}ONa$, becomes in great measure converted into ethyl oxalate, and, conversely, ethyl oxalate is transformed into methyl oxalate by dissolving it in methyl alcohol, and adding a minute quantity of sodium methoxide.

430. **Esters from Polyhydric Alcohols.**—*Glycol esters* are very numerous, because either one or both of the OH groups in $C_2H_4(OH)_2$ may be exchanged, and two different acid radicles may be introduced. None of them, however, as yet, possesses any practical importance.

431. **Glycerol Esters** or **Propenyl Salts.**—These compounds are even more

numerous than those derived from glycol, since each of the three OH groups in $C_3H_5(OH)_3$ may be exchanged for a different acid radicle.

The glyceryl chlorides are known as *chlorhydrins*. *α-Monochlorhydrin*, $CH_2Cl{\cdot}CHOH{\cdot}CH_2OH$, and *α-dichlorhydrin*, $CH_2Cl{\cdot}CHOH{\cdot}CH_2Cl$, are prepared by saturating glycerol with HCl, heating for several hours at 100° C., neutralising with Na_2CO_3, and extracting with ether. On fractionating the ethereal solution the dichlorhydrin distils first (b.-p. 174° C.). They are liquids heavier than water, in which the mono- is more soluble than the di-chlorhydrin. The *β*-chlorhydrins, $CH_2OH{\cdot}CHCl{\cdot}CH_2OH$ and $CH_2OH{\cdot}CHCl{\cdot}CH_2Cl$, are both obtained from allyl alcohol, the former by action of HClO, the latter by action of Cl. *Trichlorhydrin* is 1 : 2 : 3-trichloropropane (*q.v.*).

Epichlorhydrin, $CH_2{\cdot}\overset{\ulcorner O \urcorner}{CH}{\cdot}CH_2Cl$ is obtained by treating α- or *β*-dichlorhydrin with alkali, which removes HCl. It is a mobile liquid smelling of chloroform and insoluble in water; sp. gr. 1.2, b.-p. 117° C. It is sometimes used as a solvent.

Sulphoglyceric acid, $C_3H_5(OH)_2SO_4H$, is formed with considerable evolution of heat, when glycerol is dissolved in strong sulphuric acid. The acid may be obtained as in the case of sulphethylic acid. It is only known in solution, being easily decomposed even by evaporation *in vacuo*.

432. **Nitroglycerine**, or *glyceryl trinitrate*, $C_3H_5(NO_3)_3$, is prepared by the action of nitric acid on glycerine—$C_3H_5(OH)_3 + 3(HNO_3) = C_3H_5(NO_3)_3 + 3H_2O$. It is a heavy oily liquid, of sp. gr. 1·6, without smell, very explosive, and poisonous. It is insoluble in water, sparingly soluble in alcohol, but soluble in ether and in methyl alcohol. When saponified by potash, it yields glycerol and potassium nitrate.

On a large scale a mixture of concentrated HNO_3 with twice its volume of strong H_2SO_4 is placed in a tank lined with lead and cooled by water circulating in leaden coils. Glycerine is sprayed into the acid, care being taken that the temperature does not rise above 30° C. The mixture is allowed to settle, when much of the nitroglycerine floats to the top and is run into water and washed. The lower layer is then run into water to separate the dissolved nitroglycerine, which sinks to the bottom. A little alkali is added to the last washing water to remove any trace of free acid remaining.

This oil is very violent in its explosive effects. If a drop of nitroglycerine be placed on an anvil and struck sharply, it explodes with a very loud report, even though not free from water, and if a piece of paper moistened with a drop of it be struck, it is blown into small fragments. On the application of a flame or of a red-hot iron to nitroglycerine, it burns quietly; and when heated over a lamp in the open air it explodes but feebly. In a closed vessel, however, it explodes at about 360° F. (182° C.) with great violence. For blasting rocks, the nitroglycerine is poured into a hole in the rock, *tamped* by filling the hole with water, and exploded by the concussion caused by a detonating fuze (see below), the effect in blasting being about five times that of an equal weight of gunpowder, and much damage has occurred from the accidental explosion of nitroglycerine in course of transport. When nitroglycerine is kept, especially if it be not thoroughly washed, it decomposes, with evolution of nitrous fumes and formation of crystals of oxalic acid: and it may be readily imagined that, should the accumulation of gaseous products of decomposition burst one of the bottles in a case of nitroglycerine, the concussion would explode the whole quantity.

Nitroglycerine, like gun-cotton, is particularly well fitted for blasting, because it will explode with equal violence whether moisture be present or not, but it has the advantage of containing enough oxygen to convert all its carbon into carbonic acid gas. On the other hand, it is very poisonous, and is said to affect the system seriously by absorption through the skin, and the gases resulting from its explosion are exceedingly acrid. Again, its fluidity prevents its use in any but downward bore-holes. To overcome these objections, and to diminish the danger of transport, several blasting compounds have been proposed, of which nitroglycerine is the basis.

Dynamite is composed of a particularly porous siliceous earth (*Kieselguhr*), obtained from Oberlohe in Hanover, impregnated with about 70 or 75 per cent. of nitroglycerine. Kieselguhr contains 63 per cent. of soluble silica, about 18 of organic matter, 11 of sand and clay, and 8 of water. It is incinerated to expel the

organic matter, and mixed with the nitroglycerine in wooden troughs lined with lead. When used in solid rock, dynamite is six or seven times as strong as blasting-powder.

Nobel's detonators for nitroglycerine contain 7 parts of mercuric fulminate and 3 parts of potassium chlorate, pressed into small copper tubes.

Blasting gelatine is made by dissolving collodion-cotton in about nine times its weight of nitroglycerine; its detonation is even more powerful than that of nitroglycerine itself. *Gelatine-dynamite* consists of 65 per cent. of thinly gelatinised nitroglycerine, 8.4 per cent. of woodmeal, 26.25 potassium nitrate, and 0.35 per cent. of soda. It is slow in detonation and is an excellent blasting-agent.

Cordite is made by incorporating 58 parts of nitroglycerine with 37 parts of gun-cotton and 19.2 parts of acetone; 5 parts of vaseline are added and after this has been mixed the compound is forced through dies, so that it assumes the form of cords, from which the acetone is allowed to evaporate.

Nitroglycerine is readily soluble in ether and in wood-naphtha, but somewhat less so in alcohol; it is re-precipitated by water from these last solutions. It becomes solid at 40° F. (4.5° C.), a circumstance which is unfavourable to its use in mining operations, partly because it is then less susceptible of explosion by the detonating fuse, and partly because serious accidents have resulted from attempts to thaw the frozen nitroglycerine by heat, or to break it up with tools. It is remarkable that, when made on the small scale, the nitroglycerine may generally be cooled down to 0° F. (−18° C.) without becoming hard. This and other observations render it probable that some other substitution-product is occasionally mixed with it.

Berthelot finds that, in the formation of nitric ether by the action of nitric acid upon alcohol, 5800 heat units are disengaged for each molecule of nitric acid entering into the reaction, whereas, in the formation of nitroglycerine, only 4300 heat units per molecule of nitric acid are disengaged. Less energy having been converted into heat in the latter case, more is stored up in the nitroglycerine, and hence its formidable effect as an explosive. In the formation of gun-cotton, each molecule of nitric acid disengaged 11,000 heat units, to which Berthelot attributes the stability and inferior explosive effect of gun-cotton in comparison with nitroglycerine.

Nitroglycerine is reconverted into glycerine by alkali sulphides with rise of temperature and separation of sulphur; $C_3H_5(NO_3)_3 + 3KHS = C_3H_5(OH)_3 + 3KNO_2 + S_3$. Compare *Gun-cotton*.

Glyceryl-phosphoric or *phosphoglyceric acid*, $C_3H_5(OH)_2PO_2(OH)_2$, is formed by the action of metaphosphoric acid on glycerol, but has only been obtained in solution. It is a product of decomposition of *lecithin* (*q.v.*).

Glyceryl arsenite, $C_3H_5{\cdot}AsO_3$, is obtained by dissolving white arsenic in glycerol, and evaporating; $4C_3H_5(OH)_3 + As_4O_6 = 4C_3H_5AsO_3 + 6HOH$. It forms a yellowish glass, fusing at 50° C. It is sometimes used for fixing aniline dyes.

Glyceryl borate, or *boroglyceride*, $C_3H_5BO_3$, is prepared from boric acid and glycerol; it is also a transparent glass, dissolving slowly in water, and has been recommended for the preservation of food.

433. By far the most important ethereal salts are the fats and oils which are mixtures of *glyceryl salts of the fatty acids*, also called *glycerides*. Like other esters the oils and fats are easily hydrolysed into the alcohol (glycerol) and the acid. When an alkali is the hydrolytic agent the alkali salt of the fatty acid, a soap, is obtained. Thus when tallow is *saponified* it yields a soap composed chiefly of alkali stearate and oleate, from the *stearin* (glyceride of stearic acid) and *olein* (glyceride of oleic acid) of which it is mainly composed:

$$(C_{17}H_{35}COO)_3C_3H_5 + 3NaOH = 3C_{17}H_{35}COONa + C_3H_5(OH)_3$$
$$(C_{17}H_{33}COO)_3C_3H_5 + 3NaOH = 3C_{17}H_{33}COONa + C_3H_5(OH)_3$$

Palmitin, the glyceride of palmitic acid, the chief constituent of palm-oil, is the other principal glyceride.

Monoformin, $C_3H_5(OH)_2{\cdot}CO_2H$, and *diformin*, $C_3H_5(OH)(CO_2H)_2$, are produced when oxalic acid is heated with glycerol, in making formic acid—

$$C_3H_5(OH)_3 + (CO_2H)_2 = C_3H_5(OH)_2{\cdot}CO_2H + CO_2 + H_2O.$$

Tri-acetin, $C_3H_5(C_2H_3O_2)_3$, is present in cod-liver oil, and may be obtained by acting on glycerol with acetic acid. *Tributyrin*, $C_3H_5(C_4H_7O_2)_3$, occurs in butter.

Tripalmitin or **palmitin**, $C_3H_5(C_{16}H_{31}O_2)_3$, is obtained from palm-oil or from Chinese wax, by pressing and crystallising from alcohol. It fuses at 46° C.

Tristearin or **stearin**, $C_3H_5(C_{18}H_{35}O_2)_3$, prepared by repeatedly recrystallising the harder natural fats, such as tallow, from their solution in ether, fuses at 63° C.

Tri-olein or **olein**, $C_3H_5(C_{18}H_{33}O_2)_3$, is obtained by cooling olive-oil to 0° C., pressing out the liquid part, dissolving this in a little alcohol, again freezing, to separate the rest of the stearin, and distilling off the alcohol. Olein is less easily decomposed by alkalies than are palmitin and stearin, and is left unaltered when olive-oil is treated with a cold concentrated solution of NaOH, which converts the palmitin and stearin into soaps and glycerol.

The three glycerides, palmitin, stearin, and olein, are found in most animal and vegetable fats. *Olive-oil* and *Chinese wax* consist almost entirely of palmitin and olein. Palm-oil contains all three. *Mutton suet* is chiefly stearin, with a little palmitin and olein. *Beef suet* contains more palmitin; these constitute *tallow*. *Lard* has a similar composition. *Human fat* contains more palmitin. *Goose fat* and *butter* contain, besides the above glycerides, those of volatile acids, such as butyric, capric, caprylic, and caproic. *Coco-nut oil* contains *trilaurin*, $C_3H_5(C_{12}H_{23}O_2)_3$.

Palmitin, *stearin*, and *olein*, may be made artificially by heating glycerol with the corresponding acids; for example—

$$C_3H_5(OH)_3 + 3HC_{18}H_{35}O_2 = C_3H_5(C_{18}H_{35}O_2)_3 + 3HOH.$$

Sulphonic Acids.

434. The ethereal salts of sulphurous acid are metameric with the compounds known as the sulphonic acids; thus, both *ethyl hydrogen sulphite* and *ethyl sulphonic acid*, have the empirical formula $C_2H_6SO_3$. The sulphonic acids, however, differ from the sulphites in that when treated with reducing-agents they yield the corresponding thio-alcohols; thus, ethyl sulphonic acid, $C_2H_5SO_3H$, yields mercaptan (ethyl thio-alcohol) C_2H_5SH. This reaction indicates that the sulphur in ethyl sulphonic acid is combined directly with the carbon of the ethyl group, for there can be no doubt that the S in mercaptan is so combined. The constitution of ethyl sulphonic acid, is therefore probably $O_2S\langle^{C_2H_5}_{OH}$, whilst that of ethyl hydrogen sulphite is $OS\langle^{OC_2H_5}_{OH}$.

When a strong solution of sodium sulphite is heated with ethyl iodide at 140° C., sodium ethyl sulphonate and sodium iodide are produced: $Na_2SO_3 + C_2H_5I = C_2H_5{\cdot}SO_2ONa + NaI$. If sodium sulphite were a salt of $SO(OH)_2$, viz., $SO(ONa)_2$, this reaction would be expected to produce ethyl sodium sulphite $SO(ONa)(OC_2H_5)$.* Since this is not the case, Na_2SO_3 must have the constitution $SO_2(ONa)Na$; this constitutes the evidence referred to on p. 222.

The sulphonic acids bear the same relationship to sulphuric acid, as the carboxylic acids bear to carbonic acid, that is, they contain an alcohol radicle or a hydrocarbon radicle in place of one of the OH groups. They are monobasic acids since they still retain one OH group. By partial reduction they generally yield *sulphinic acids*, which bear the same relationship to the $SO(OH)_2$ form of sulphurous acid as the sulphonic acids bear to sulphuric acid.

The sulphonic acids are also produced by oxidation of the mercaptans.

* *Ethyl sulphite*, $SO(OC_2H_5)_2$, is prepared by the action of $SOCl_2$ on alcohol. When heated with one equivalent of NaOH it yields ethyl sodium sulphite; when this is treated with an acid with a view to removing the Na, it is decomposed, so that ethyl hydrogen sulphite has not been prepared.

Ethyl sulphinic acid, $C_2H_5{\cdot}SO{\cdot}OH$, is obtained as a zinc salt by the action of SO_2 on a cooled ethereal solution of zinc ethide; $Zn(C_2H_5)_2 + 2SO_2 = (C_2H_5{\cdot}SO_2)_2Zn$. The acid itself is a syrupy liquid. It might be regarded as propionic acid, $C_2H_5{\cdot}CO{\cdot}OH$, in which tetravalent sulphur is substituted for the carbon of the carboxyl.

Ethyl-sulphonic acid, $C_2H_5{\cdot}SO_2{\cdot}OH$, is produced when ethyl-sulphinic acid, mercaptan, ethyl polysulphides, and ethyl sulphocyanate are oxidised by nitric acid; also from C_2H_5I and Na_2SO_3, as stated above. Ethyl-sulphonic acid is an oily liquid of sp. gr. 1.3, and may be crystallised by cooling. It forms very soluble salts, which are not easily decomposed by heat. By oxidation with HNO_3 it yields ethyl hydrogen sulphate.

Ethionic acid has already been noticed (p. 535). It is a mixed ethereal salt and sulphonic acid from glycol, $CH_2(OSO_3H){\cdot}CH_2(SO_3H)$. By hydrolysis the ethereal salt portion is split off, H_2SO_4 and *isethionic acid* or *hydroxy-ethyl sulphonic acid*, $CH_2(OH){\cdot}CH_2(SO_3H)$, being produced.

It is characteristic of closed-chain compounds (at all events such as contain a benzene nucleus) that they readily yield sulphonic acids when heated with strong sulphuric acid (p. 549). These are very useful for preparing other compounds, *e.g.*, phenols (*q.v.*), and, on account of their solubility, for use as dye-stuffs. They yield chloranhydrides (p. 191) when treated with PCl_5.

When benzene is warmed with H_2SO_4 conc., *benzene sulphonic acid*, $C_6H_5{\cdot}SO_2OH$, is produced; if fuming acid be employed the three (chiefly 1 : 3) *benzene di-sulphonic acids*, $C_6H_4(SO_2OH)_2$, are produced. Naphthalene may be similarly sulphonated to produce isomeric *naphthalene mono-* and *di-sulphonic acids*. Sulphonic acids of most benzene hydrocarbon derivatives are easily obtainable; some of these will receive passing mention later.

NITRO-COMPOUNDS.

435. The ethereal salts of nitrous acid are metameric with the nitro-substituted hydrocarbons; thus, ethyl nitrite, $C_2H_5O{\cdot}N : O$, is metameric with nitro-ethane, $C_2H_5{\cdot}NO_2$. The difference in constitution represented by these two formulæ is justified as follows: (1) When an ethereal nitrite is treated with an alkali, it is readily converted into an alcohol and an alkali nitrite: this shows that the compound is a true ethereal salt of nitrous acid, the formula for which, as already shown (p. 101), is probably $HO{\cdot}N : O$. (2) When a nitro-hydrocarbon is treated with a reducing-agent, it yields an amine (*e.g.*, $C_2H_5{\cdot}NH_2$), a compound which, since it contains only C, H, and N, must contain the N attached directly to carbon. On the other hand, when an ethereal nitrite is treated with a reducing-agent it yields the corresponding alcohol and ammonia; since the alcohols contain O attached directly to carbon, the ethereal nitrite probably also contains O attached directly to carbon, in which case the N is probably not attached directly to carbon, a conclusion confirmed by the ease with which the C and N are parted in these compounds by saponification. The nitro-compounds may be regarded as derived from nitric acid in the same way that the sulphonic acids are derived from sulphuric acid.

The *nitro-paraffins* are produced by the inter-action of silver nitrite and alkyl iodides, *e.g.*, $C_2H_5I + AgNO_2 = C_2H_5{\cdot}NO_2 + AgI$.* The *nitro-*

* This reaction would seem to show that silver nitrite is derived from a form of nitrous acid in which H was attached directly to N, thus, $H{\cdot}NO_2$. It may be that nitrites exist in two forms, as has been argued for sulphites (p. 648). It is necessary to add, however, that in most cases much ethereal nitrite is produced, together with the nitro-paraffin, by this method.

***hydrocarbons of the benzene series*, however, result from the direct action of nitric acid on the hydrocarbons (p. 549).**

When the hydrocarbon has a side-chain, strong nitric acid yields a nucleal nitro-compound, but dilute acid introduces the nitro-group into the side-chain. While it is easy to introduce one or two nitro-groups into an aromatic nucleus, the direct introduction of the third is difficult, and more than three have not been introduced.

The nitro-paraffins can be primary, secondary, or tertiary like all other open-chain hydrocarbon substitution-products. The three forms have the same structure as the three forms of alcohols, NO_2 being substituted for OH (p. 567). The distinctive behaviour of the three kinds with nitrous acid has been given at p. 569. The primary and secondary nitro-paraffins contain hydrogen attached to the same carbon atom as that to which the NO_2 is attached; the close proximity of the NO_2 to the H imparts an acid character to the latter, so that this may be exchanged for metals, such compounds as $CH_3{\cdot}CHNa{\cdot}NO_2$ and $(CH_3)_2 : CNa{\cdot}NO_2$ being produced by the action of alcoholic soda on the nitro-paraffin; compare the influence of two COOH group on a CH_2 group (p. 587). The nitro-aromatic compounds having the nitro-group or groups in the nucleus are of a tertiary character, but when the group or groups are in the side-chain all three kinds may exist.*

Nitro-methane boils at 101° C.; hydrolysis (by strong HCl at 150° C.) converts it into formic acid and hydroxylamine. *Nitro-ethane* boils at 113° C.; it gives a blood-red colour with ferric chloride, and burns with a luminous flame. Both are heavier than water.

Trichloronitromethane or **chloropicrin** or *nitro-chloroform*, CCl_3NO_2, is a product of the joint action of nitric acid and chlorine on many hydrocarbon derivatives. It is best obtained by heating picric acid (*q.v.*) with chloride of lime, when it distils over as a heavy liquid (sp. gr. 1.69), boiling at 112° C. and possessed of a tear-exciting odour. Nascent H reduces it to methylamine, HCl and H_2O.

Nitrobenzene, $C_6H_5{\cdot}NO_2$, has already been noticed (p. 540). It is prepared on the large scale by slowly running a mixture of 1280 lbs. of strong HNO_3 and 1790 lbs. of strong H_2SO_4 into 1000 lbs. of benzene contained in a cast-iron cylinder well cooled by water, and provided with an agitator; after some 8 or 10 hours the process is complete and the product is washed with water. If the temperature be allowed to rise above 50° C. during the preparation of nitrobenzene, the three *dinitrobenzenes* are produced. Since they may be regarded as being formed from the further nitration of nitrobenzene, it is only in accordance with the general rule (p. 547) that 1 : 3-dinitrobenzene is the chief product: this crystallises in pale yellow needles and melts at 90° C. The 1 : 2- and 1 : 4-dinitrobenzenes are colourless and melt at 116° and 172° C. respectively. The three can be separated by fractional crystallisation from alcohol. They yield the corresponding *nitranilines*, $C_6H_4(NH_2)(NO_2)$, and *diamidobenzenes* or *phenylenediamines*, $C_6H_4(NH_2)_2$ when reduced. The 1 : 2-derivative differs from the others in the comparative ease with which one nitro-group can be exchanged for other radicles (*e.g.*, for OH, forming 1 : 2-nitrophenol, $C_6H_4(OH)(NO_2)$, when heated with hot alkalies).

By nitrating toluene, 1 : 2- and 1 : 4-*nitrotoluene*, $C_6H_4(CH_3)(NO_2)$, are mainly produced; the former is a liquid boiling at 223° C., the latter a solid melting at 54° C. and boiling at 237° C. 1 : 3-*Nitrotoluene* has m.-p. 16° C., and b.-p. 230° C.

Trinitrotertiarybutyltoluene, $(NO_2)_3C_6H(CH_3)C(CH_3)_3[(NO_2)_3 : CH_3 : C(CH_3)_3 = 2 : 4 : 6 : 1 : 3\frac{1}{2}]$, is obtained by nitrating various butyltoluene derivatives, and is sold as *artificial musk*.

α-*Nitronaphthalene*, $C_{10}H_7NO_2$, is produced by boiling naphthalene in glacial acetic acid with strong nitric acid; it crystallises in yellow prisms, melts at 61° C. and boils at 304° C. It is used for making dyes and for destroying the fluorescence of paraffin oils when these are used to adulterate vegetable oils. It is soluble in alcohol but not in water.

* The salts of the primary and secondary nitro-compounds appear to be derived from a tautomeric form, the *isonitro-compound*, *e.g.*, $CH_3{\cdot}CH : NO_2H$; for when treated with acids they yield a free nitro-compound which at first shows reactions differing from those of the original nitro-compound, such as a colouration with Fe_2Cl_6; afterwards it resumes the usual properties.

Other nitro-derivatives will be considered under the classes of bodies from which they are derived.

VIII. ORGANO-MINERAL COMPOUNDS.

436. The importance of these compounds resides mainly in the light they throw upon the theory of valency and in the fact that many of them are volatile without decomposition, thus yielding evidence of the atomic weight of their elements (p. 318). They may be regarded as formed on the type of the chlorides of the mineral elements by the substitution of hydrocarbon radicles for the chlorine. Those containing alkyl groups (*alkides*) have been best studied, and it has been found that in the case of the compounds from the more electro-negative elements the subtraction of one or more alkyl groups from the saturated compound yield monovalent or polyvalent radicles. For example, tin methide, $Sn(CH_3)_4$, is a saturated alkyl derivative of Sn^{IV}; by treatment with iodine, one CH_3 is removed and $Sn(CH_3)_3I$ is produced. This is the iodide of a monovalent radicle, $Sn(CH_3)_3$, which behaves like an alkali metal, forming a powerful base, $Sn(CH_3)_3OH$, obtained by treating the iodide with NaOH. Like other monovalent radicles, such as CH_3, $Sn(CH_3)_3$ cannot exist alone, but is known in its double form, $Sn_2(CH_3)_6$, like C_2H_6. When two alkyl groups are removed, the divalent radicle, $Sn(CH_3)_2$, is produced; this resembles a divalent metal and forms a base $Sn(CH_3)_2O$; like CH_2 it exists alone only in the form $Sn_2(CH_3)_4$.

The most important method of producing these compounds is by the action of metals on the monohalogen substituted hydrocarbons. The typical case is that of zinc ethide, which will be considered first.

Zinc alkides.—*Zinc ethyl* or *zinc ethide*, $Zn(C_2H_5)_2$, is prepared in accordance with the equation $Zn_2 + 2C_2H_5I = Zn(C_2H_5)_2 + ZnI_2$.

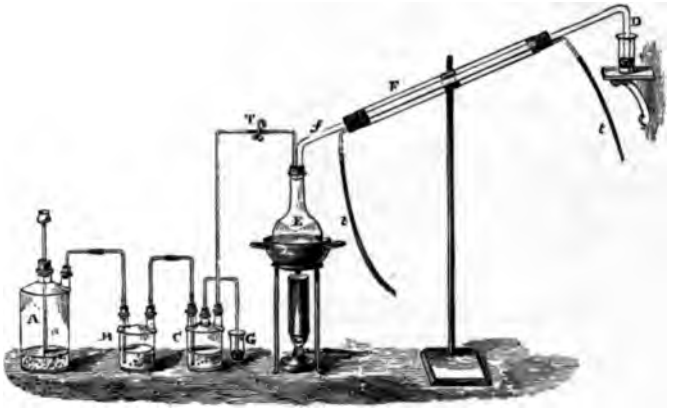


Fig. 278.—Preparation of zinc ethyl.

Fifty grams of bright, freshly granulated and well-dried zinc are placed in a flask E (Fig. 278) connected with a CO_2 apparatus A, the gas from which is dried by strong H_2SO_4 in bottles B and C. The flask is also connected with the tube *f* of condenser F, the other end of which is sealed by mercury in D. The apparatus having been filled with CO_2, the cork of the flask is removed, and 25 grams of

ethyl iodide (perfectly free from moisture) are introduced, the cork being then replaced.* CO_2 is again passed for a short time, and then cut off by closing the nipper-tap (T), when the gas escapes through the mercury seal (G). A gentle heat is then applied by a water-bath to the flask (E) till the ethyl iodide boils briskly, the vapour being condensed in the tube (*f*), and running back into the flask. In about five hours the conversion is complete, and the iodide ceases to distil. The nipper-tap (T) is again opened, and a slow current of CO_2 is passed, the position of the condenser (F) is reversed (Fig. 279), and the tube (*f*) is connected by the cork (K) with the short test-tube (O); the longer limb of a very narrow siphon (I) of stout tube passes through a second perforation in the cork (K), the shorter limb

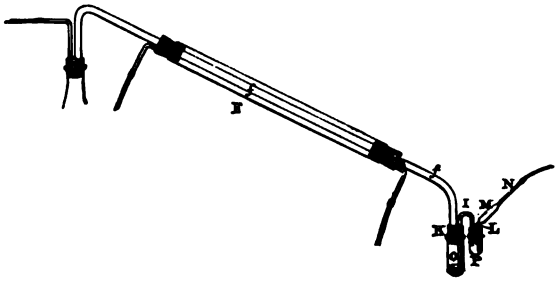


Fig. 279.—Collection of zinc ethyl.

passing into the very short test-tube (P), the cork of which is also furnished with the short piece of moderately wide tube (L). For receiving and preserving the zinc ethyl, a number of small tubes are prepared of the form shown in Fig. 280. The long narrow neck (R) of one of these is passed down the short tube (L) to the bottom of P, the other end (N) of the tube being connected with an apparatus for passing dry CO_2. The whole of the apparatus being filled with this gas, the nipper-tap is closed, and the flask (E) heated on a sand-bath, so that the zinc ethyl may distil over, a slow stream of carbonic acid gas being constantly passed into P, the excess escaping through L. When enough zinc ethyl has collected in the tube (O), a blowpipe flame is applied to the narrow tube (N), which is drawn off and sealed; the siphon tube (I) is then gradually pushed down, so that its longer limb may be sufficiently immersed in the zinc ethyl, and the nipper-tap (T, Fig. 278) is opened, when the pressure of the carbonic acid gas forces over a part of the zinc ethyl into the tube (P). By heating the tube (M) with a spirit-lamp, so as to expel part of the gas, allowing it to cool, it will become partly filled with zinc ethyl, and may be withdrawn and quickly sealed by the blow-pipe. The spontaneous inflammability of the zinc ethyl, and its easy decomposition by water, render great care necessary in its preparation. If an alloy of zinc with one-fourth its weight of sodium be employed, the conversion may be effected in an hour.

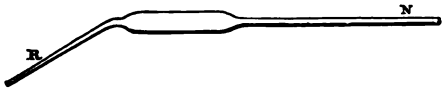


Fig. 280.

The reaction in the preparation of zinc ethide really occurs in two stages; when the ethyl iodide ceases to distil, the flask contains *zinc iodo-ethide*, $ZnIC_2H_5$, as a crystalline solid, decomposed by a higher temperature into zinc ethide and zinc iodide; $2ZnIC_2H_5 = Zn(C_2H_5)_2 + ZnI$. The action is more rapid if the zinc be polarised by copper. To effect this, CuO is reduced by heating it in a tube in a current of hydrogen or coal-gas, and 10 grams of it are mixed with 90 grams of zinc-filings in a 300 c.c. flask, which is then heated with continual shaking, until the mixture forms grey granular masses. After cooling, 87 grams of ethyl iodide are added, and the mixture heated to about 90° C. with the reversed condenser.

* The process is said to be much accelerated if about $\frac{1}{50}$th of zinc ethyl is dissolved in the ethyl iodide.

till no more liquid distils back, which requires about 15 minutes; the rest of the operation is conducted as described above, using a sand-bath or an oil-bath.

Zinc ethide is a colourless liquid of peculiar odour, sp. gr. 1.18, b.-p. 118° C. In contact with air, it inflames spontaneously, burning with a bright greenish-blue flame, emitting a white smoke of ZnO. If a piece of porcelain be depressed upon the flame, a deposit of metallic zinc is formed, surrounded by a ring of oxide, yellow while hot and white on cooling. Dissolved in ether and treated with oxygen, it yields *zinc ethoxide*, $Zn(OC_2H_5)_2$, a white powder. Water decomposes it readily, ethane or ethyl hydride being evolved; $Zn(C_2H_5)_2 + H_2O = ZnO + 2(C_2H_5{\cdot}H)$. When NH_3 is passed into the solution of zinc ethide in ether, C_2H_6 is evolved, and a white precipitate of zinc amide deposited—

$$Zn(C_2H_5)_2 + 2NH_3 = 2(C_2H_5{\cdot}H) + Zn(NH_2)_2.$$

Zinc ethide and ethyl iodide, dissolved in ether and heated to 170° C., yield butane, or di-ethyl; $Zn(C_2H_5)_2 + 2C_2H_5I = ZnI_2 + 2(C_2H_5)_2$. Heated with sulphur, zinc ethide is converted into *zinc mercaptide*, $Zn(SC_2H_5)_2$, the analogue of zinc ethoxide and zinc hydroxide. Zinc ethide is much used in organic research, especially for effecting the substitution of C_2H_5 for Cl, Br, I, or OH.

Dissolved in ether and heated with Na in a sealed tube, zinc ethide exchanges one-third of its Zn for Na, forming a crystalline compound of zinc ethide with sodium ethide, $3Zn(C_2H_5)_2 + Na_2 = 2(Zn(C_2H_5)_2{\cdot}NaC_2H_5) + Zn$. When this is treated with dry CO_2, zinc ethide distils, and sodium propionate remains; $NaC_2H_5 + CO_2 = C_2H_5{\cdot}CO_2Na$.

Zinc methide, or *zinc methyl*, $Zn(CH_3)_2$, prepared from methyl iodide, like zinc ethide, which it resembles, boils at 46° C., and has a more powerful odour, producing irritation. It is more energetic in its reactions than zinc ethide, and is decomposed, with inflammation and explosion, by water, yielding methane.

437. **Boron Alkides.**—*Boron methide*, $B(CH_3)_3$, formed by the action of a strong ethereal solution of $Zn(CH_3)_2$ upon ethyl borate, $2(C_2H_5)_3BO_3 + 3Zn(CH_3)_2 = 2B(CH_3)_3 + 3Zn(O{\cdot}C_2H_5)_2$, is a gas with an intolerably pungent, tear-exciting odour, liquefied by three atmospheres pressure. When issuing very slowly into the air, it undergoes partial oxidation, with phosphorescence, but when it comes rapidly into contact with air, it burns with a green flame, remarkable for the immense quantity of large flakes of carbon which it emits.

Boron ethide, or *triborethyl*, $B(C_2H_5)_3$, is prepared by passing vapour of boron chloride into zinc ethide; $2BCl_3 + 3Zn(C_2H_5)_2 = 2B(C_2H_5)_3 + 3ZnCl_2$. It is a colourless liquid of irritating odour, and insoluble in water. Its sp. gr. is 0.69, and it boils at 95° C. It inflames spontaneously in air, burning with a green flame, and explodes in contact with pure oxygen. Water slowly converts it into $B(C_2H_5)_2OH$, another spontaneously inflammable liquid. By gradual oxidation in air it becomes $BC_2H_5(OC_2H_5)_2$, decomposed by water, into alcohol and *ethyl-boric acid*, $BC_2H_5(OH)_2$, which is a volatile crystalline body, subliming in scales like boric acid, and having a very sweet taste and a pleasant smell; it is very soluble in water, alcohol, and ether.

438. **Silicon Alkides.**—*Silicon methide*, $Si(CH_3)_4$, produced by the action of $SiCl_4$ upon $Zn(CH_3)_2$, is a liquid lighter than water, burning in air, and producing a white smoke of silica. It is stable in water, and boils at 30° C. *Silicon ethide*, or $Si(C_2H_5)_4$, obtained by a similar process, resembles the methide, but boils at 153° C. In its chemical relations it resembles the paraffin hydrocarbons, and is sometimes called *silico-nonane*, the ninth member of the paraffin series, C_9H_{20}, in which silicon is exchanged for an atom of carbon. When acted on by chlorine, it yields $SiC_8H_{19}Cl$; when this is heated with potassium acetate, in alcoholic solution, it yields the acetate $SiC_8H_{19}{\cdot}C_2H_3O_2$, and by heating this with alcoholic solution of potash, it is converted into *silico-nonyl alcohol*, $SiC_9H_{19}{\cdot}OH$, boiling at 190° C.

By acting on ethyl orthosilicate, $Si(OC_2H_5)_4$, with zinc ethide and sodium, *silicon triethyl ethoxide* $Si(C_2H_5)_3{\cdot}OC_2H_5$, *silicon diethyl-diethoxide*, $Si(C_2H_5)_2(OC_2H_5)_2$, and

silicon ethyl-triethoxide, $SiC_2H_5(OC_2H_5)_3$, may be produced. When the last named is heated with acetyl chloride, it yields *silicon ethyl trichloride*, $SiC_2H_5Cl_3$, which is converted by water into *silico-propionic acid*, $C_2H_5{\cdot}SiOOH$, a solid, feeble acid. *Silico-acetic acid*, $CH_3{\cdot}SiOOH$, is also known.

439. **Phosphines.**—These compounds being formed on the type of PH_3, the analogue of NH_3, are primary, secondary, and tertiary, like the alkylamines, as explained in the next section.

Tri-ethyl phosphine, $P(C_2H_5)_3$, a tertiary phosphine, is prepared by very gradually dropping PCl_3 into a solution of zinc ethide in ether, in a retort connected with a receiver filled with CO_2; a very violent action occurs—$2PCl_3 + 3Zn(C_2H_5)_2 = 3ZnCl_2 + 2P(C_2H_5)_3$. The upper layer of the distillate contains the excess of PCl_3 and ether, the lower being a compound of $ZnCl_2$ with tri-ethyl phosphine, which may be separated by careful distillation with KOH in a retort filled with H. It is also obtained by heating phosphonium iodide with alcohol, in a sealed tube, to 180° C.; $PH_4I + 3C_2H_5OH = P(C_2H_5)_3{\cdot}HI + 3HOH$; the hydriodide is distilled with KOH. Tri-ethyl phosphine is a liquid of strong odour, sp. gr. 0.81, and b.-p. 127° C. It behaves like a divalent metal of the calcium group, absorbing O from the air, becoming hot and exploding below 100° C. It forms salts with the acids and its oxide, $P(C_2H_5)_3O$, is a very stable crystalline substance, obtained, together with ethane, by distilling *tetrethyl phosphonium iodide* with potash; $P(C_2H_5)_4I + KOH = P(C_2H_5)_3O + KI + C_2H_5{\cdot}H$. The tetrethyl-phosphonium iodide is obtained by heating ethyl iodide with P in a sealed tube; $4C_2H_5I + P_2 = P(C_2H_5)_4I + PI_3$. By decomposing its aqueous solution with Ag_2O, the *tetrethyl phosphonium hydroxide*, $P(C_2H_5)_4OH$, is produced, a strongly alkaline substance, which may be crystallised and is comparable with the hydroxides of the alkali metals.

The primary and secondary phosphines, *ethyl phosphine* $P(C_2H_5)H_2$, and *di-ethyl phosphine*, $P(C_2H_5)_2H$, are prepared by heating PH_4I with C_2H_5I and ZnO, in a sealed tube for some hours; crystalline compounds of zinc iodide with the hydriodides of ethyl phosphine and di-ethyl phosphine are first formed;

$$2PH_4I + 2C_2H_5I + ZnO = H_2O + ZnI_2 + 2(P(C_2H_5)H_2.HI), \text{ and}$$
$$PH_4I + C_2H_5I + ZnO = H_2O + ZnI_2 + P(C_2H_5)_2H.HI.$$

These are decomposed by distillation with water out of contact with air, when the phosphines distil over.

Ethyl phosphine is a feebly basic liquid, boiling at 25° C., having an intolerable odour, insoluble in water. Di-ethyl phosphine is also liquid, but boils at 85° C., and is more strongly basic. Both compounds, being composed upon the PCl_3 model, are disposed to unite with other bodies to form compounds upon the PCl_5 model. When oxidised by nitric acid, they yield, respectively, *ethyl phosphinic acid*, $PO(C_2H_5)(OH)_2$, and *di-ethyl phosphinic acid*, $PO(C_2H_5)_2OH$, composed upon the model of orthophosphoric acid, $PO(OH)_3$, by the substitution of ethyl for hydroxyl.

Tri-ethyl phosphine combines violently with methyl iodide, forming $P(C_2H_5)_3CH_3{\cdot}I$, which yields an alkaline hydroxide when decomposed with water and silver oxide.

Tri-ethyl phosphine combines with sulphur, evolving heat, and forming $P(C_2H_5)_3S$, which crystallises in needles from solution in hot water. It also combines energetically with CS_2, forming a fine red crystalline compound soluble in alcohol, and forming a test for CS_2 in coal gas.

The *methyl phosphines* are similar to the ethyl compounds and are similarly prepared.

Phenylphosphine (*phosphaniline*), $PH_2 \cdot C_6H_5$, is prepared by the action of HI on phosphenyl chloride, $PC_6H_5Cl_2$; it is a liquid of intense and repellent odour, boils at 160° C., and absorbs oxygen from the air to form the soluble crystalline *phenylphosphine oxide*, $C_6H_5PH_2O$.

Phosphenyl chloride, $PC_6H_5Cl_2$, obtained when mercury diphenyl $(C_6H_5)_2Hg$, is heated with PCl_3, is a liquid which combines with Cl to form crystals of the *tetrachloride*, $PC_6H_5Cl_4$. When treated with water it yields *phenyl hypophosphorous acid* (*phosphenylous acid*), $C_6H_5 \cdot PHO(OH)$. From the tetrachloride, *phenyl phosphinic acid* (*phosphenylic acid*), $C_6H_5 \cdot PO(OH)_2$, is similarly prepared.

Phosphenyl chloride and phenylphosphine react to form *phosphobenzene*, $C_6H_5 \cdot P : P \cdot C_6H_5$, the analogue of azobenzene, $C_6H_5 \cdot N : N \cdot C_6H_5$.

440. **Arsines.** While the alkyl derivatives of NH_3 and PH_3 are strongly basic, those of AsH_3 are not. Moreover, only the tertiary and secondary derivatives are known. The divalent radicles like $As(CH_3)_2$, however, give rise to salt-forming oxides, and the radicles themselves exist in double form.

Trimethyl arsine, $As(CH_3)_3$, or Kd., is obtained by the action of $AsCl_3$ on zinc methide. It is a strong-smelling liquid, boiling at about 70° C., and resembling $P(C_2H_5)_3$, but not forming salts with the acids.

Arsen-dimethyl, or kakodyl, $As(CH_3)_2$, has a special interest as having been one of the first bodies recognised as a compound radicle capable of behaving like an elementary substance. The formula $As(CH_3)_2$ represents only one volume of vapour, so that it must be doubled to represent a molecule, conveniently termed *dikakodyl*. The oldest compound of kakodyl is the *dikakodyl oxide*, Kd_2O, or *alcarsin*, or *arsenical alcohol*, named, after its discoverer, *Cadet's fuming liquid*, and obtained by distilling a mixture of equal weights of white arsenic and potassium acetate—

$$As_4O_6 + 8CH_3CO_2K = 2[As(CH_3)_2]_2O + 4CO_2 + 4K_2CO_3.$$

The distillate has a strong odour of garlic, and takes fire spontaneously, owing to the presence of dikakodyl. It is received in water, when it sinks to the bottom; sp. gr. 1.46, b.-p. 120° C. It combines with acids to form salts, and dissolves in alcohol, the solution giving, with alcoholic mercuric chloride, a crystalline precipitate of $Kd_2O.2HgCl_2$. By distilling this precipitate with strong HCl in a retort filled with CO_2, *kakodyl chloride*, KdCl is obtained as a heavy spontaneously inflammable liquid, of terrible odour. When this is heated to 100° C. with zinc in an atmosphere of CO_2, a compound of $ZnCl_2$ with kakodyl is produced, and on treating this with water *dikakodyl* separates as a heavy oily liquid which boils at 170° C. It inflames spontaneously in air, and when its vapour is passed through a tube heated to 400° C., it is decomposed—$As_2(CH_3)_4 = 2CH_4 + C_2H_4 + As_2$. When slowly oxidised by air, it is converted into Kd_2O, which is afterwards converted, in presence of water, into *kakodylic acid*, $KdO \cdot OH$, or *dimethyl-arsenic acid*, $AsO(CH_3)_2 \cdot OH$, *i.e.*, arsenic acid, $AsO(OH)_3$, in which two OH groups are exchanged for $(CH_3)_2$. This acid is best prepared by oxidising Kd_2O with mercuric oxide in presence of water—$Kd_2O + 2HgO + H_2O = 2KdO_2H + Hg_2$. It crystallises from the aqueous solution, and is a stable acid.

Sulphur dissolves in dikakodyl, forming Kd_2S, a colourless liquid of unpleasant smell, which behaves like an alkali sulphide. Kd_2S_2 is a solid which may be crystallised from alcohol.

Kakodyl cyanide, KdCN, prepared by distilling kakodyl chloride with mercuric cyanide, forms lustrous prismatic crystals, m.-p. 37° C., b.-p. 140°. It is nearly insoluble in water, but dissolves in alcohol. Its vapour is very poisonous.

Kakodyl trichloride, $As(CH_3)_2Cl_3$, is composed upon the model of $AsCl_5$, whilst the *chloride*, $As(CH_3)_2Cl$, is formed after $AsCl_3$. The chloride ignites in Cl, but, if it be dissolved in CS_2, the action of Cl converts it into crystals of the trichloride. When this is heated, it evolves CH_3Cl, and a heavy irritating liquid distils, which is *arsenmethyl dichloride*, $AsCH_3Cl_2$, boiling at 133° C., and soluble in water without decomposition. By evaporating the solution with Na_2CO_3, and extracting the residue with alcohol and crystallising, *arsenmethyl oxide*, $AsCH_3O$, is obtained. The crystals smell like assafœtida. Mercuric oxide in the presence of water, converts the oxide into *methyl-arsinic acid*, $AsCH_3O(OH)_2$.

With methyl iodide, dikakodyl yields kakodyl iodide and *tetramethyl-arsonium iodide*, $As_2(CH_3)_4 + 2CH_3I = As(CH_3)_2I + As(CH_3)_4I$; this last, when decomposed by moist silver oxide, yields the corresponding hydroxide, $As(CH_3)_4OH$, which is strongly alkaline, and may be crystallised.

Dimethylarsine, $(CH_3)_2AsH$, is a spontaneously inflammable liquid (b.-p. 36° C.), obtained by the action of Zn and HCl on an alcoholic solution of KdCl.

The ethyl compounds of arsenic are in every respect similar to the methyl compounds.

441. **Antimony Alkides.**—Antimony forms compounds with the hydrocarbon radicles, composed upon the models $SbCl_3$ and $SbCl_5$.

Stibio-trimethyl, or *trimethyl stibine*, $Sb(CH_3)_3$, is prepared by distilling in a current of CO_2 methyl iodide with the potassium antimonide obtained by strongly heating tartar-emetic; $3CH_3I + K_2Sb = 3KI + (CH_3)_3Sb$. The powdered antimonide must be mixed with sand to moderate the action. The product is a garlic-smelling liquid, of sp. gr. 1.52, and boiling at 80° C. It is insoluble in water, but dissolves in ether. By the slow action of air it is converted into $Sb(CH_3)_3O$, but is liable to take fire. It combines with chlorine and iodine, forming $Sb(CH_3)_3Cl_2$ and $Sb(CH_3)_3I_2$, which may be crystallised, and are formed upon the model of $SbCl_5$. Stibio-trimethyl combines at once with methyl iodide, forming $Sb(CH_3)_4I$ as a white solid, crystallising in six-sided plates from hot water. When decomposed by Ag_2O in presence of water, it yields a strong alkali, *tetramethyl-stibonium hydroxide*, $Sb(CH_3)_4OH$, which may be crystallised, and forms crystallisable salts.

Stibio-pentamethyl, $Sb(CH_3)_5$, composed on the model of $SbCl_5$, is obtained by distilling stibio-trimethyl iodide with zinc methide.

Stibio-tri-ethyl, or *tri-ethyl stibine*, $Sb(C_2H_5)_3$, is obtained like stibio-trimethyl: or by acting on antimonious chloride with zinc ethide: $2SbCl_3 + 3Zn(C_2H_5)_2 = 2Sb(C_2H_5)_3 + 3ZnCl_2$. It resembles the methyl compound, but boils at 158° C. It is remarkable for behaving like a metal; even decomposing hydrochloric acid and liberating hydrogen: $Sb(C_2H_5)_3 + 2HCl = Sb(C_2H_5)_3Cl_2 + H_2$. The chloride is an oily liquid smelling like turpentine. Its salts behave like those of the alkalies.

Bismuth tri-ethyl, $Bi(C_2H_5)_3$, is prepared by acting on ethyl iodide with an alloy of potassium and bismuth. It is a spontaneously inflammable liquid which is very unstable, depositing bismuth even below 100° C., and exploding at 150°. As might be expected from the non-existence of $BiCl_5$, bismuth tri-ethyl shows no disposition to combine directly with the halogens, its derivatives being formed on the model of $BiCl_3$.

442. **Lead Alkides.**—The compounds of lead with alcohol radicles are not composed upon the model of the stable chloride, $PbCl_2$, but upon that of $PbCl_4$, which is not known in the pure state.

Lead tetramethyl, $Pb(CH_3)_4$, is formed by the action of zinc-methyl upon lead chloride; $2Zn(CH_3)_2 + 2PbCl_2 = 2ZnCl_2 + Pb(CH_3)_4 + Pb$; it distils at 110° C., and has the sp. gr. 2.03. It has a faint odour, is unaffected by air, and is insoluble in water. Heated with HCl—$Pb(CH_3)_4 + HCl = Pb(CH_3)_3Cl + CH_4$. The chloride is crystalline, and may be sublimed; by reaction with KI it gives colourless crystals of $Pb(CH_3)_3I$, and when this is distilled with potash, $Pb(CH_3)_3OH$ is obtained as a strongly alkaline body smelling like oil of mustard.

Lead tetrethyl, $Pb(C_2H_5)_4$, and its derivatives resemble the methyl compounds.

Lead tri-ethyl, $Pb(C_2H_5)_3$, is obtained by the action of ethyl iodide upon an alloy of sodium and lead. This combines with iodine in alcoholic solution, forming $Pb(C_2H_5)_3I$, which yields a hydroxide, like the corresponding methyl compound.

443. **Mercury Alkides.**—*Mercuric methide*, $Hg(CH_3)_2$, may be obtained by the reaction between mercuric chloride and zinc methide, but better by dissolving

one part of sodium in one hundred parts of mercury, and adding the amalgam, by degrees, to methyl iodide mixed with one-tenth of its volume of ethyl acetate, the action of which has not yet been explained. On distillation, the mercuric methide is obtained as a colourless liquid which is one of the heaviest known, its sp. gr. being 3.07, so that glass floats in it. It is unchanged by exposure to air, but gives off a faint odour which is very poisonous. It boils at 95° C., and burns with a bright flame. With strong HCl, $Hg(CH_3)_2 + HCl = HgCH_3Cl + CH_3{\cdot}H$.

Mercuric ethide, $Hg(C_2H_5)_2$, is prepared like the methide. It has the sp. gr. 2.4, and boils at 159° C. Its vapour is decomposed at 200° C. into Hg and butane, but with strong H_2SO_4 it gives ethane.

Mercury ethyl chloride, HgC_2H_5Cl, is obtained by acting on mercuric ethide with mercuric chloride dissolved in alcohol; $Hg(C_2H_5)_2 + HgCl_2 = 2HgC_2H_5Cl$; this shows it to be composed upon the mercuric type, $HgCl_2$, and not derived from the mercurous compound $Hg_2(C_2H_5)_2$, corresponding with Hg_2Cl_2. The chloride is insoluble in water, but crystallises from alcohol, and is easily sublimed. Silver oxide converts it into the *mercury ethyl hydroxide*, HgC_2H_5OH, a caustic alkaline liquid which blisters the skin. The iodide, HgC_2H_5I, obtained by treating $Hg(C_2H_5)_2$ with I_2, is remarkably stable, crystallising from hot caustic soda, almost without decomposition. It is hardly soluble in water or alcohol.

Mercury diphenyl, $(C_6H_5)_2Hg$, is formed when Na-amalgam acts on C_6H_5Br. It is a crystalline solid (m.-p. 120° C.), subliming almost unchanged, insoluble in water, and sparingly soluble in alcohol and ether, but soluble in benzene. When heated, in a sealed tube, with $HgCl_2$ and alcohol, it yields *mercury-phenyl chloride*, HgC_6H_5Cl, which, with silver hydroxide, yields *mercury-phenyl hydroxide*, $HgC_6H_5{\cdot}OH$, a crystalline strongly alkaline base.

444. **Tin Alkides.**—*Tin tetramethide*, $Sn(CH_3)_4$, composed upon the model of stannic chloride, $SnCl_4$, is obtained by the action of an alloy of Sn, Hg, and Na upon CH_3I. It boils at 78° C. By the action of iodine, one CH_3 group is removed, and *tin trimethyl iodide*, $Sn(CH_3)_3I$, obtained; this, acted on by NaOH, yields $Sn(CH_3)_3OH$, a sparingly soluble, crystalline, volatile, alkaline base.

When CH_3I is heated to 160° C., in a sealed tube, with tin-foil, *tin dimethyl iodide*, $Sn(CH_3)_2I_2$ is formed. It crystallises in yellow prisms soluble in water; NH_3 gives a white precipitate of the base $Sn(CH_3)_2O$ with the solution.

Tin tetrethide, or *stannic ethide*, $Sn(C_2H_5)_4$ (b.-p. 181° C.), prepared by distilling stannic chloride with zinc ethide, is remarkably stable, even when boiled with sodium. It is not precipitated by H_2S.

Like the tetramethide, it yields the iodides $Sn(C_2H_5)_2I_2$ and $Sn(C_2H_5)_3I$. By treatment with Na these undergo nucleal condensation yielding a mixture of $Sn_2(C_2H_5)_4$ and $Sn_2(C_2H_5)_6$, which may be separated by alcohol in which the former, *stannous ethide*, or *tin diethide*, is insoluble. It is a liquid of sp. gr. 1.56, decomposed when heated; $Sn_2(C_2H_5)_4 = Sn(C_2H_5)_4 + Sn$. It is an unsaturated compound, absorbing oxygen from the air, and forming $Sn(C_2H_5)_2O$, which forms crystalline salts, like $Sn(C_2H_5)_2(NO_3)_2$.

Tin hexethide, $Sn_2(C_2H_5)_6$, boils at 270° C., decomposing into $Sn(C_2H_5)_4$ and Sn.

445. *Aluminium methide*, $Al(CH_3)_3$, and the corresponding *ethide* are obtained by decomposing mercuric methide and ethide by Al. They are spontaneously inflammable liquids, violently decomposed by water, yielding $Al_2(OH)_6$ and methane or ethane. Their vapour densities are known.

Magnesium methide, $Mg(CH_3)_2$, and *ethide* are prepared by decomposing CH_3I or C_2H_5I with Mg, when a solid iodide, $MgCH_3I$, is first formed, which is decomposed when distilled in CO_2; $2MgCH_3I = Mg(CH_3)_2 + MgI_2$. They are spontaneously inflammable liquids, yielding $Mg(OH)_2$ and CH_4 or C_2H_6, with water.

Organo-mineral compounds similar to those which have been described are formed by other alcohol radicles and benzene hydrocarbon residues, and mixed compounds are obtainable.

Thus, $Sn(CH_3)_2(C_2H_5)_2$ may be produced by the action of zinc methide upon $Sn(C_2H_5)_2Cl_2$; and $Sn(CH_3)_3C_2H_5$ is formed by zinc ethide with $Sn(CH_3)_3Cl$.

IX. AMMONIA-DERIVATIVES.

446. The organic compounds classed under this head are derived from NH_3 by substitution of radicles for H, and are in many cases very nearly related to the organo-mineral compounds, since such compounds as $P(CH_3)_3$, $As(CH_3)_3$, $Sb(CH_3)_3$, $B(CH_3)_3$, are formed upon the type of PH_3, AsH_3, SbH_3, and BH_3, which are nearly allied to NH_3; but the strongly alkaline character of ammonia impresses special characters upon the bodies derived from it. These may be divided into—

(1) *Amines* or *ammonia-bases*, formed by the substitution of alcohol radicles for the hydrogen in ammonia, such as $NH_2{\cdot}CH_3$, $NH(CH_3)_2$, $N(CH_3)_3$. This class also includes the *ammonium bases*, formed by the substitution of alcohol radicles for hydrogen in ammonium hydroxide, NH_4OH, such as $N(CH_3)_4OH$. All these are basic, many of them powerfully so.

(2) *Amides*, derived from ammonia by the substitution of acid radicles for hydrogen, such as $NH_2(CH_3CO)$, $NH(CH_3CO)_2$, $N(CH_3CO)_3$. These may also be regarded as formed from acids by the exchange of 1, 2, or 3 OH groups from the COOH groups of the acid for $(NH_2)'$, $(NH)''$, and N''' respectively. They are only slightly basic compounds, since the acid radicle has nearly neutralised the basic character of the parent ammonia.

(3) *Amido-acids*, derived from acids by the substitution of $(NH_2)'$ for H in the hydrocarbon residue, such as $CH_2(NH_2){\cdot}COOH$ from $CH_3{\cdot}COOH$. These are both basic and acid in character.

A compound containing the group NH_2 is known as an *amide*, one containing NH is an *imide*, whilst one containing N, attached to carbon only, is a *nitrile*.

Amines or Ammonia-bases and Ammonium-bases.

447. These are called *primary*, *secondary*, *tertiary*, or *quaternary*, accordingly as one, two, three, or four atoms of H in NH_3 have been exchanged. The quaternary bases can only be derived from NH_4OH.

Amines or ammonia bases.			Ammonium-bases.
Primary or Amido-bases.	Secondary or Imido-bases.	Tertiary or Nitrile-bases.	Quaternary bases.
NH_2R'	NHR'_2 NHR''	NR'_3 NR'''	NR'_4OH

Amines are also distinguished as *monamines*, *diamines*, and *triamines*, accordingly as they are derived from one, two, or three molecules of ammonia. The amines in the above table are examples of monamines, and the following are examples of the other two classes:

	Diamines.	Triamines.
Primary	N_2H_4R''	N_3H_6R'''
Secondary	$N_2H_2R_2''$; $N_2R_2''R_2'$	$N_3H_3R'''R_2'$; $N_3H_3R'R''R'''$
Tertiary	N_2R_3'' ; $N_2R''R_4'$	N_3R_3''' ; $N_3R'''R_6'$.

The secondary and tertiary amines may be either simple or mixed, that is to say, the radicles R may be either the same or different.

Generally speaking the amines share the properties of ammonia, forming crystalline salts with acids, which, however, differ from the ammonium salts in being soluble in alcohol. The amines containing open-chain radicles are somewhat more basic than NH_3, and the basicity increases with the number of radicles, NHR_2 being a stronger base than NH_2R, and NR_3 stronger than either. The amines containing aromatic radicles may have the NH_2, NH, or N group attached either to the closed-chain, like $NH_2{\cdot}C_6H_5$ or $NH:(C_6H_5)_2$, or to the side-chain, like $NH_2{\cdot}CH_2{\cdot}C_6H_5$ and $NH:(CH_2{\cdot}C_6H_5)_2$; those of the latter class behave in every respect like the fatty amines, but those in which the nitrogen is attached to the closed-chain show slight differences, due to the fact that *a closed-chain nucleus is always somewhat more acidic than an open-chain nucleus;* thus, phenylamine ($C_6H_5{\cdot}NH_2$) is less basic than ethylamine ($C_2H_5{\cdot}NH_2$), because the basic properties of ammonia have been more neutralised by phenyl than by ethyl. For the same reason, the nucleal aromatic amines show some relationship to the amides and amido-acids (p. 658); for instance, they readily undergo the diazo-reaction (p. 680) characteristic of amides and amido-acids. Hence some chemists term the aromatic amines amido-compounds. The difference here defined is precisely similar to that between the alcohols and phenols (see *Phenols*).

The most generally applicable method for preparing the amines consists in reducing the corresponding nitro-compounds with nascent hydrogen. Since the nitro-compounds are more easily obtained from closed-chain than from open-chain hydrocarbons, this method is most frequently used for preparing aromatic amines; $C_6H_5NO_2 + H_6 = C_6H_5NH_2 + 2H_2O$.

The cyanides of hydrocarbon radicles are convertible into amines by treatment with nascent H; $C_2H_5{\cdot}CN + H_4 = C_2H_5{\cdot}CH_2{\cdot}NH_2$.

The open-chain amines can be prepared by heating the hydrocarbon halides with ammonia in alcohol, but the aromatic amines cannot be similarly produced from the nucleal halogen-substituted benzene hydrocarbons. For example, *methylamine*, NH_2CH_3, *dimethylamine*, $NH(CH_3)_2$, and *trimethylamine*, $N(CH_3)_3$, in the form of their hydriodides, and *tetramethyl ammonium iodide*, $N(CH_3)_4I$, are all obtained when a strong solution of ammonia in alcohol is heated with methyl iodide for some hours, in a sealed tube at 100° C. The reactions which occur may be represented by the following equations ($Me = CH_3$):

(1) $NH_3 + MeI = NH_2Me{\cdot}HI$;
(2) $2NH_3 + 2MeI = NHMe_2HI + NH_4I$;
(3) $3NH_3 + 3MeI = NMe_3{\cdot}HI + 2NH_4I$;
(4) $4NH_3 + 4MeI = NMe_4I + 3NH_4I$.

The NH_4I being nearly insoluble in alcohol separates at once and the hydriodides of the three amines crystallise on cooling, leaving the NMe_4I in solution. They are distilled with KOH into a receiver cooled in ice, when a mixture of NMe_3, $NHMe_2$, and a little NH_2Me is condensed, much of the last escaping as gas with the NH_3 from the NH_4I. Any NMe_4I not previously separated by crystallisation remains in the retort, as it is not decomposed by KOH. The mixed amines are then digested with ethyl oxalate, when the NMe_3 is not acted on, and may be distilled off. The methylamine is converted into methyloxamide, and the dimethylamine into ethyl dimethyloxamate ($E = C_2H_5$)—

$$2NH_2Me + \begin{matrix}COOE\\COOE\end{matrix} = \begin{matrix}CONHMe\\CONHMe\end{matrix} + 2EOH;$$

$$NHME_2 + \begin{matrix}COOE\\COOE\end{matrix} = \begin{matrix}CONMe_2\\COOE\end{matrix} + EOH.$$

Water at 0° dissolves the last-named compound, and leaves the methyloxamide undissolved. On distillation with potash, the methyloxamide yields potassium oxalate and methylamine; $(CONHMe)_2 + 2KOH = (COOK_2) + 2NH_2Me$: and the ethyl dimethyloxamate yields potassium oxalate, dimethylamine, and alcohol—

$$C_2O_2(NMe_2)(OE) + 2KOH = (COOK)_2 + NHMe_2 + EOH.$$

The primary and secondary amines in which there is still ammoniacal H are capable of many of the reactions of NH_3; the tertiary amines, having no ammoniacal H, are less reactive.

On this depend the reactions which *distinguish between primary, secondary, and tertiary amines.* The amine is treated with nitrous acid (or, what comes to the same thing, $NaNO_2$ is added to a strong solution of the amine hydrochloride). A primary amine yields the corresponding alcohol *with evolution of nitrogen;* $C_2H_5{\cdot}NH_2 + HO{\cdot}N:O = C_2H_5{\cdot}OH + N_2 + HOH$. (*Cf.* the action of NH_3 on HNO_2.) A secondary amine yields a *nitrosamine, which separates in oily drops*—

$$(C_2H_5)_2NH + HO{\cdot}N:O = (C_2H_5)_2N{\cdot}NO + HOH.$$

A tertiary amine is unchanged.

A primary amine can also be distinguished by the *carbylamine reaction.* The hydrochloride is warmed with chloroform and alcoholic KOH; the characteristically disagreeable odour of a carbylamine (*q.v.*) is produced; $C_2H_5{\cdot}NH_2 + CHCl_3 + 3KOH = C_2H_5{\cdot}N \vdots C + 3KCl + 3HOH.$

A nitrosamine can be further recognised by Liebermann's *nitroso-reaction*: the suspected compound is mixed with phenol and H_2SO_4 conc. A nitroso-compound gives a dark green solution, becoming red when diluted and blue when made alkaline.

Another method of investigating the constitution of an amine, is to heat its alcoholic solution with methyl iodide in a sealed tube: a tertiary amine yields a substituted ammonium iodide by direct union with methyl iodide: $N(C_2H_5)_3 + CH_3I = N(C_2H_5)_3{\cdot}CH_3I$; a secondary amine yields an ammonium iodide containing two methyl groups; $NH(C_2H_5)_2 + 2CH_3I = HI + N(C_2H_5)_2(CH_3)_2I$: a primary amine yields an ammonium iodide containing three methyl groups. $NH_2(C_2H_5) + 3CH_3I = N(C_2H_5)(CH_3)_3I + 2HI$. See, also, *Mustard-oil reaction.*

With organic chloranhydrides the primary and secondary amines react to form amides in which the H of the NH_2 group is exchanged for hydrocarbon-radicles (*cf.* p. 667); thus, with acetyl chloride, methylamine, NH_2CH_3 reacts to form *acetmethylamide*—$CH_3CO{\cdot}Cl + NH_2CH_3 = CH_3CO{\cdot}NHCH_3 + HCl$: dimethylamine, $NH(CH_3)_2$, yields *acetdimethylamide*, $CH_3CO{\cdot}N(CH_3)_2$. The secondary amines also react with inorganic chloranhydrides to form similar substituted amides (*c.f.* p. 265); thus, from $POCl_3$ and $NH(CH_3)_2$ is obtained $PO[N(CH_3)_2]_3$. Primary amines are apt to give substituted imides, such as $CH_3N:SO$ from NH_2CH_3 and $SOCl_2$.

448. **Monamines.**—Simple alkylamines are prepared as described above for methylamines. Mixed alkylamines are obtained by heating the amine of one radicle with the iodide of another (see above). The amines of methyl and ethyl are here described as typical.

Methylamine, NH_2CH_3, is a gas (b.-p. −6° C.) resembling ammonia, but more combustible and more soluble in water; in this it surpasses all gases, one volume of water dissolving 1150 volumes of methylamine. The solution is strongly alkaline. In its reactions with metallic salts it resembles ammonia, but it dissolves aluminium hydroxide and will not

dissolve the hydroxides of Cd, Ni, and Co. Its behaviour with acids and with $PtCl_4$ is similar to that of ammonia.

Heated to redness it yields hydrocyanic acid, HCN, and NH_4CN. Potassium converts it into potassium cyanide—$NH_2CH_3 + K = KCN + H_2$. Conversely, methylamine is formed by the action of nascent hydrogen on hydrocyanic acid; $HCN + H_4 = NH_2CH_3$. It is also produced by distilling methyl isocyanate with potash (see *Cyanogen*). Methylamine occurs in the fruit of *Mercurialis* (dog-mercury), a plant of the order *Euphorbiaceæ*. Several of the alkaloids yield it when distilled with potash.

Dimethylamine, $NH(CH_3)_2$, is a gas boiling at 7° C., and resembling methylamine. It has been found in wood-spirit and in guano.

Trimethylamine, $N(CH_3)_3$, is obtained on a large scale by distilling the *vinasses* obtained in refining beet-root sugar, which corresponds with the molasses from cane-sugar, but is not fit for food. It contains sugar, by fermentation of which alcohols are obtained, and substances containing nitrogen,* which furnish ammonia and amines derived from the alcohols when distilled.

By neutralising the distillate with HCl, the hydrochlorides of ammonia, trimethylamine, &c., are obtained. The NH_4Cl, being less soluble, is crystallised out and the $N(CH_3)_3HCl$ is distilled with lime, when trimethylamine comes off as a gas which may be absorbed by water. The solution also contains dimethylamine, ethylamine, propylamine, and butylamine. It has been used for converting KCl into K_2CO_3, by a process resembling the ammonia-soda process (p. 315), which depends on the fact that $NaHCO_3$ is less soluble in water than is NH_4Cl; but $KHCO_3$ has about the same solubility as NH_4Cl, so that trimethylamine, whose hydrochloride is much more soluble, is substited for ammonia.

Trimethylamine boils at 3.5° C.; it has a fish-like smell, is inflammable, and mixes easily with water. It forms salts by direct combination with acids, like ammonia. It is not unfrequently found in plants, as in the flowers of hawthorn, pear, and wild cherry, and in arnica and ergot of rye. It also occurs in the roe of the herring, and may be obtained by distilling herring-brine with lime. It is often found in the products of distillation of animal substances, together with amines containing other alcohol-radicles. Bones, when distilled, yield trimethylamine, methylamine, ethylamine, propylamine, and butylamine. The putrefaction of flour and other nitrogenous substances furnishes these ammonia-derivatives. The hydrochloride of trimethylamine is employed for making methyl chloride on the large scale, as described on p. 633.

449. **Tetramethylammonium hydroxide**, $N(CH_3)_4OH$, is prepared by decomposing the iodide with AgOH; $NMe_4I + AgOH = NMe_4OH + AgI$. The iodide (tetramethylium iodide), obtained as already described, forms prismatic crystals, and may be purified by crystallisation from water, in which it is rather sparingly soluble. Evaporated *in vacuo*, the solution of the hydroxide yields a crystalline deliquescent mass, which acts like a caustic alkali, and absorbs CO_2 from the air. When heated, it yields methyl alcohol and trimethylamine; $NMe_4OH = NMe_3 + MeOH$. The ammonium bases form salts with acids in the same way as the alkali hydroxides; thus, $NMe_4OH + HNO_3 = NMe_4NO_3 + H_2O$; $2NMe_4OH + H_2SO_4 = (NMe_4)_2SO_4 + 2H_2O$. These are not decomposed by potash, even on boiling—*a distinction between the salts of amines and ammonium bases.*

* Particularly *betaine* (*Beta vulgaris*, beet), or *trimethyl glycocine*, $C(CH_3)_3 \cdot NH_2CO_2CH_3$.

450. The *ethylamines* may be prepared by the action of ammonia on ethyl iodide and may be separated from each other in the same way as the methylamines.

They are prepared on a large scale by the action of NH_3 upon the impure ethyl chloride obtained as a secondary product in the manufacture of chloral. This is heated for an hour in a closed vessel with a saturated alcoholic solution of NH_3. The volatile matters are then distilled off, and the hydrochlorides crystallised; on decomposing these with strong soda solution, the three ethylamines form an oily layer on the surface. They are separated as described under the methylamines.

Ethylamine, $NH_2C_2H_5$, is an ammoniacal inflammable liquid, of sp. gr. 0.696, and boiling-point 18.7° C. It mixes with water in all proportions. It is a stronger base than ammonia, and dissolves alumina, though it does not easily dissolve cupric hydroxide. Its salts resemble those of ammonia, *e.g.*, $NH_2E.HCl$, $(NH_2E)_2H_2SO_4$, $(NH_2E.HCl)_2PtCl_4$.

Di-ethylamine, $NH(C_2H_5)_2$, is also an ammoniacal liquid, boiling at 56° C., and mixing easily with water. Unlike ethylamine, it does not dissolve $Zn(OH)_2$. When its hydrochloride is distilled with potassium nitrite and a little water, *ethylnitrosamine* is obtained; this contains the group ·NO in place of the imido-hydrogen atom, $(C_2H_5)_2N{\cdot}NO$. Di-ethylamine nitrite is probably first formed and then decomposed—$(C_2H_5)_2NH.HONO = (C_2H_5)_2N{\cdot}NO + HOH$. Ethylnitrosamine is a yellow aromatic liquid insoluble in water, of sp. gr. 0.95 and b.-p. 177° C. Nascent H reconverts it into di-ethylamine—$2NE_2NO + H_4 = 2NE_2H + H_2O + N_2O$. When it is dissolved in hydrochloric acid, and HCl gas passed into the solution, it yields nitrosyl chloride and di-ethylamine hydrochloride—

$$NE_2NO + 2HCl = NE_2H.HCl + NOCl.$$

Tri-ethylamine, $N(C_2H_5)_3$, differs from the other amines in having a pleasant smell, and being sparingly soluble in water. It boils at 89° C. Its reaction is strongly alkaline, and it resembles ammonia in its action upon metallic salts, except that it dissolves alumina, and scarcely dissolves silver oxide, which is readily soluble in ammonia.

451. **Tetrethylammonium hydroxide**, $N(C_2H_5)_4{\cdot}OH$, is prepared like the methyl compound, which it much resembles, but crystallises rather more easily. In its chemical behaviour, it is very similar to potassium hydroxide, but it produces, in chromic salts, a precipitate of chromic hydroxide, which does not dissolve in excess. When heated to 100° C., it does not yield alcohol, but ethane, water, and tri-ethylamine; $N(C_2H_5)_4{\cdot}OH = C_2H_4 + H_2O + N(C_2H_5)_3$. If it be heated with ethyl iodide, alcohol and *tetrethylammonium iodide* are formed; $NE_4OH + EI = EOH + NE_4I$. The iodide may be obtained by the combination of $N(C_2H_5)_3$ with C_2H_5I, just as NH_4I is formed by NH_3 and HI, the combination producing heat. It crystallises in cubes like the alkali iodides, and becomes brown, when exposed to air, from the formation of the *triodide*, NE_4I_3. It is very soluble in alcohol and in water, but is insoluble in solution of potash, which precipitates it from the aqueous solution, but without decomposing it. When heated, tetrethylammonium iodide undergoes dissociation, like ammonium chloride, yielding ethyl iodide, which distils over, and is followed by tri-ethylamine, these afterwards combining to reproduce the iodide.

By heating a primary amine, NH_2R', successively with R''I, KOH, R'''I, KOH and $R^{IV}I$, a mixed quaternary ammonium iodide, of the form $NR'R''R'''R^{IV}I$, may be obtained. The importance of such compounds to the theory of stereoisomerism has been noted at p. 607.

452. *Chloramines* are formed from primary and secondary amines by action of Cl or HClO on amines, just as NCl_3 is formed from NH_3, only here there are only one or two H atoms to be exchanged for Cl. *Iodamines* and *bromamines* are also known.

The *nitramines*, such as *methylnitramine*, $CH_3NH{\cdot}NO_2$, were originally supposed to be nitro-derivatives of the primary and secondary amines in which NO_2 was substituted for the ammoniacal H. This view has been traversed, and certain isomeric forms have been discovered.

453. **Phenylamine, or aniline, or *amidobenzene*, $C_6H_5{\cdot}NH_2$, is**

prepared from nitrobenzene, $C_6H_5{\cdot}NO_2$, by reducing it with metallic iron in conjunction with acetic or hydrochloric acid.

On the large scale, the operation is conducted in a cast-iron retort provided with an agitator and a vertical condenser. 20 parts of fine cast-iron filings, some water, and 1 part of HCl are introduced into the retort, and 20 parts of nitrobenzene are allowed to flow slowly in, with constant stirring. Steam is blown into the retort through the hollow agitator, and the action continued until no more nitrobenzene volatilises and runs back from the condenser, whereupon high-pressure steam is blown in. Aniline and water distil over, the former sinking to the bottom, and the water, which retains a little aniline, being used to furnish steam for the next operation. The aniline is purified by distillation, and the iron residues are sent to the blast furnaces. In this method the HCl is only required to start the reaction, which may be represented by the equation,

$$4C_6H_5NO_2 + 4H_2O + Fe_9 = 4C_6H_5NH_2 + 3Fe_3O_4.$$

The process requires care, because, if the action becomes too violent, benzene and ammonia are produced; $C_6H_5{\cdot}NO_2 + H_6 = C_6H_5{\cdot}H + NH_3 + 2H_2O$.

On the small scale, tin is more convenient than iron. Granulated tin is placed in a retort with inverted condenser, and covered with strong HCl; nitrobenzene is added in small portions, and when the action has moderated, the mixture is

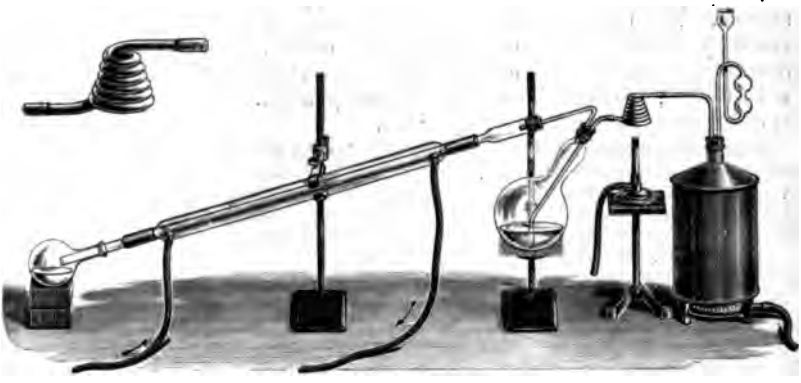


Fig. 281.—Distillation in a current of steam.

boiled till all the nitrobenzene has disappeared; $C_6H_5NO_2 + 3SnCl_2 + 6HCl = C_6H_5NH_2 + 3SnCl_4 + 2H_2O$; the liquid is decanted from the excess of tin, when it deposits, on cooling, a crystalline compound of aniline hydrochloride with stannic chloride; $(C_6H_5NH_2HCl)_2.SnCl_4$. By distilling this with excess of potash or soda in a current of superheated steam the aniline is set free. The apparatus for this purpose is shown in Fig. 281. The steam generated in the boiler passes through the coil of copper tube, which is heated by the burner, into the distillation flask, carrying the aniline with it through the condenser.

Nitrobenzene may also be converted into aniline by dissolving it in alcohol, saturating the solution with NH_3, then with H_2S gas repeatedly, as long as the latter is acted on; $C_6H_5NO_2 + 3H_2S = C_6H_5NH_2 + 2H_2O + S_3$. The liquid is decanted from the S, and the alcohol and ammonium sulphide distilled off in a water-bath; the mixture of aniline and any unaltered nitrobenzene is treated with HCl, which dissolves only the aniline; this may be liberated by distillation with potash.

Since commercial benzene contains toluene and other hydrocarbons, the aniline prepared from it contains toluidine and other bases. To purify it, the crude aniline is boiled with glacial acetic acid, in a flask with a reversed condenser, when it is converted into *acetanilide*, $C_6H_5{\cdot}NH{\cdot}C_2H_3O$. This is distilled, washed with carbon bisulphide, and recrystallised from water till its melting-point is 115° C., when pure aniline may be obtained from it by boiling with NaOH—

(1) $NH_2{\cdot}C_6H_5 + C_2H_3O{\cdot}OH = NH{\cdot}C_6H_5{\cdot}C_2H_3O + HOH$;
(2) $NH{\cdot}C_6H_5{\cdot}C_2H_3O + NaOH = NH_2{\cdot}C_6H_5 + NaO{\cdot}C_2H_3O$.

Aniline was originally obtained by distilling indigo, either alone or with caustic alkalies, and was named from *anil*, the Portuguese name of indigo. It is also found in coal tar, and in the products of distillation of bones and peat.

Properties of aniline.—Colourless when pure, but generally of a yellow or even brown colour, having a characteristic rather ammoniacal smell; sp. gr. 1.03, and boiling-point 184° C. When shaken with water, it appears almost insoluble, but the water dissolves about $\frac{1}{30}$th of its weight of aniline, and the latter about $\frac{1}{20}$th of its weight of water. It is easily soluble in alcohol and ether, which collects it from an aqueous solution. It has no alkaline reaction, and is less strongly basic than the alkylamines, though it precipitates hydroxides of Zn, Al, and Fe. Most of its salts crystallise easily. The *hydrochloride*, $C_6H_5{\cdot}NH_2.HCl$, is commercially known as *aniline-salt*. The *oxalate*, $(C_6H_7N)_2.H_2C_2O_4$, is rather sparingly soluble in water. Aniline has the rare property of dissolving indigo.

Many oxidising-agents produce intensely coloured products with aniline. The usual test for it is solution of chloride of lime (bleaching-powder), which gives a purple-violet colour, changing to brown. Solutions of aniline give a bright green precipitate, $(C_6H_5NH_2)_2CuSO_4$, with $CuSO_4$. By Caro's reagent (a persulphate in strong H_2SO_4) aniline is oxidised to *nitrosobenzene*, $C_6H_5{\cdot}NO$.

Substitution products of aniline are obtained by the reduction of the corresponding nitro-compounds; thus 1 : 2-chloronitro-benzene, $C_6H_4Cl{\cdot}NO_2$, will yield 1 : 2-*chloraniline*, $C_6H_4Cl{\cdot}NH_2$. By the action of chlorine or bromine water on aniline, the *trichloranilines* and *tribromanilines* are produced, the latter form the white precipitate which bromine-water gives with aniline.

Nitranilines, or *nitrophenylamines*, $C_6H_4NO_2{\cdot}NH_2$, are obtained by the partial reduction of the dinitro-benzenes with NH_4HS (p. 663). The presence of the acidic NO_2 or Cl greatly reduces the basic character of aniline. Thus *dinitraniline* is neutral, and *trinitraniline*, $C_6H_2(NO_2)_3{\cdot}NH_2$, is acidic in properties.

Aniline-sulphonic acid, or 1 : 4-*amidobenzenesulphonic acid*, or *sulphanilic acid*, $C_6H_4(SO_3H){\cdot}NH_2$, is obtained by heating aniline with twice its weight of fuming sulphuric acid at 180° C. until SO_2 is given off. When the liquid is diluted, the acid is precipitated. Sulphanilic acid is the parent substance of several dyes.

454. **Alkylanilines.**—Aniline, being a primary amine, may be converted into secondary and tertiary amines by action of iodides of other radicles. Thus, *methylaniline*, $C_6H_5{\cdot}NHCH_3$, and *dimethylaniline*, $C_6H_5N(CH_3)_2$, are obtained by the action of methyl iodide on aniline, or by heating methyl alcohol with aniline hydrochloride, in a closed vessel, at 250° C., when the hydrochlorides of the methyl bases, and water, are produced. Dimethylaniline is also prepared on a large scale by the action of methyl chloride on a heated mixture of aniline and caustic soda—

$$2CH_3Cl + C_6H_5NH_2 + 2NaOH = C_6H_5N(CH_3)_2 + 2NaCl + 2H_2O.$$

They are liquids boiling at about 190° C., and used in the manufacture of certain aniline dyes. Such *alkylanilines* are more basic than aniline, and behave generally like phenyl-substituted open-chain amines. The dialkylanilines, however, react with nitrous acid, notwithstanding that they are tertiary amines (p. 660). The products are *iso-nitroso-derivatives*—*i.e.*, the NO group is attached directly to C; thus, *isonitroso-dimethylaniline* is $C_6H_4(NO){\cdot}N(CH_3)_2$.

455. **Diphenylamine**, or *phenylaniline*, $NH(C_6H_5)_2$, is a secondary amine obtained by heating aniline hydrochloride with aniline at 250° C., in a closed vessel from which the NH_3 is allowed to escape from time to time—

$$C_6H_5{\cdot}NH_2HCl + C_6H_5{\cdot}NH_2 = NH(C_6H_5)_2 + NH_3{\cdot}HCl;$$

the excess of aniline employed decomposes the NH_4Cl, so that a mixture of aniline hydrochloride and diphenylamine is left; on adding water, the latter is left undissolved. It is a crystalline solid, soluble in alcohol and ether, and having feeble basic properties. It melts at 54° C. and boils at 310° C. When acted on by HNO_2,

three atoms of the phenyl hydrogen are exchanged for NO_2, producing *hexanitrodiphenylamine*, $NH(C_6H_2(NO_2)_3)_2$, an acid which combines with ammonia forming $N(NH_4)(C_6H_2(NO_2)_3)_2$, an orange dye, *aurantia*.

Diphenylamine is used as a delicate test for nitrous acid, with which it gives a deep blue colour in strong sulphuric acid.

The ammonia-hydrogen in aniline may be evolved by dissolving potassium in the base, when $NHK{\cdot}C_6H_5$ and $NK_2C_6H_5$ are produced. By acting on the latter with phenyl bromide (bromobenzene) the tertiary amine, *triphenylamine*, $N(C_6H_5)_3$, is produced ; $NK_2C_6H_5 + 2C_6H_5Br = N(C_6H_5)_3 + 2KBr$. This compound is not basic ; it is insoluble in water, but may be crystallised from ether.

456. The three **toluidines**, or *amido-toluenes*, $C_6H_4CH_3{\cdot}NH_2$, are metameric with methyl-aniline and benzylamine. They are prepared by reducing the nitrotoluenes, just as aniline is prepared from nitrobenzene. *Orthotoluidine* resembles aniline; sp. gr. 1.003, and boiling-point 197° C. It becomes pink in air. Chloride of lime gives it a brown colour, which is changed to red by acids. *Metatoluidine* is a liquid of sp. gr. 0.998, and boiling at 199° C. *Paratoluidine*, which forms about 35 per cent. of commercial toluidine, is crystalline, fusing at 45° C. and boiling at 198° C. It is sparingly soluble in water, and is feebly alkaline; alcohol and ether dissolve it. It is not coloured by chloride of lime. Its basic properties are weak. Its oxalate is insoluble in ether, which dissolves orthotoluidine oxalate. When methylaniline, hydrochloride is heated to 350° C., it is converted into the isomeric paratoluidine hydrochloride; $C_6H_5{\cdot}NHCH_3,HCl = C_6H_4(CH_3){\cdot}NH_2,HCl$. This *migration* of a group from a side-chain into the nucleus is frequently noticed.

Commercial *aniline-oil* is never free from toluidine, so that it gives a brown colour with chloride of lime, as well as the violet due to aniline. Ether extracts the toluidine brown, which becomes pink by shaking the ethereal layer with acetic acid. *Aniline-oil for blue* is approximately pure aniline ; *aniline-oil for red* contains equimolecular proportions of aniline and orthotoluidine; *aniline-oil for safranine* is a mixture of aniline and orthotoluidine recovered during the manufacture of magenta.

Commercial toluidine is obtained by reducing the product obtained by nitrating toluene (p. 650), and consists of ortho- and para-toluidine. The latter is the stronger base of the two, so that when the mixture is partially saturated with H_2SO_4 and distilled, it remains in the retort as sulphate.

457. **Xylidines**, $C_6H_3(CH_3)_2{\cdot}NH_2$. These are six in number, and are metameric with dimethylaniline. Commercial xylidine is chiefly *amidoparaxylene*, and is prepared by heating dimethylaniline hydrochloride, when a change occurs analogous to that involved in the conversion of methylaniline hydrochloride into paratoluidine hydrochloride (*r.s.*) ; $C_6H_5{\cdot}N(CH_3)_2$, $HCl = C_6H_3(CH_3)_2{\cdot}NH_2$, HCl. It is used for making dyes.

Benzylamine, $C_6H_5{\cdot}CH_2NH_2$, is produced by the action of benzyl chloride on NH_3 in alcoholic solution ; $C_6H_5{\cdot}CH_2Cl + NH_3 = C_6H_5{\cdot}CH_2NH_2$, HCl. By distilling the hydrochloride with KOH, it is obtained as a colourless liquid, boiling at 187°. It is metameric with toluidine, but is easily soluble in water, and is a strongly alkaline base. *Dibenzylamine*, $(C_6H_5{\cdot}CH_2)_2NH$, and *tribenzylamine*, $(C_6H_5{\cdot}CH_2)_3N$, are formed in the same reaction as benzylamine.

α-Naphthylamine, or *naphthalidine*, $C_{10}H_7{\cdot}NH_2$, or *amido-naphthalene*, prepared from α-nitro-naphthalene like aniline from nitro-benzene, forms colourless needles, smelling of mice ; m.-p. 50° C., b.-p. 300° C. It dissolves sparingly in water, but easily in alcohol, and forms well-crystallised salts, which give, with ferric chloride, a blue precipitate, changing to purple *oxynaphthylamine*, $C_{10}H_9NO$. It is also obtained by heating aniline with pyromucic acid, $CO_2 + H_2O$ being eliminated. *β-naphthylamine* gives no colour with ferric chloride.

458. **Diamines.**—The commonest open-chain diamines are those which are derived from ethylene. If *ethylene diamine*, $C_2H_4(NH_2)_2$, be

regarded as glycol in which NH_2 is substituted for OH, it will be seen that *alcohol-amines*, such as $C_2H_4(OH)(NH_2)$, can exist; these are monamines, and have been called *hydramines*, or *hydroxyamines*. Thus, $C_2H_4(OH)(NH_2)$ is *hydroxy-ethylamine*. The diamines are diacid bases, *i.e.*, they are equivalent to $2NH_3$ in their relation to acids.

Etylene diamine, $CH_2NH_2{\cdot}CH_2NH_2$ (b.-p. 116° C.). Ethylene bromide is heated with an alcoholic solution of NH_3 at 100° C.; $2NH_3 + C_2H_4Br_2 = C_2H_4(NH_2)_2{\cdot}2HBr$. The hydrobromides of *diethylene diamine*, $N_2H_2(C_2H_4)_2''$ (b.-p. 145° C.), and *triethylene diamine*, $N_2(C_2H_4)_3''$ (b.-p. 210° C.), are produced at the same time. The three diamines are liberated by KOH and fractionally distilled.

Ethylene diamine smells feebly of ammonia, but dissolves in water and is alkaline. It is also formed by reducing cyanogen with $HCl + Sn$; $CN{\cdot}CN + H_4 = CH_2NH_2{\cdot}CH_2NH_2$. Nitrous acid converts it into ethylene oxide, though glycol is probably first formed.

Diethylene diamine has the structure $NH\begin{<}{CH_2{\cdot}CH_2}{CH_2{\cdot}CH_2}\end{>}NH$ and is identical with *piperazine* (see *Pyrazine*) which is used as a remedy for gout, since it readily dissolves uric acid. It melts at 104° C., and boils at 145° C.

Hydroxy-ethylamine, $CH_2OH{\cdot}CH_2NH_2$, is obtained by the action of ammonia on ethylene chlorhydrin; $C_2H_4(OH)Cl + 2NH_3 = C_2H_4(OH)NH_2 + NH_4Cl$. The secondary monamine, *dihydroxy-ethylamine*, $(C_2H_4OH)_2NH$, is produced at the same time, and when this is dehydrated it yields *morpholine*, $O\begin{<}{CH_2{\cdot}CH_2}{CH_2{\cdot}CH_2}\end{>}NH$, a base closely allied to morphine.

Two important animal products have been shown to be ammonium bases connected with the hydramines; these are *choline*, which occurs in bile, egg-yolk, and the brain; and *neurine*, which is also obtained from the brain. The latter is typical of the class of poisonous substances resulting from decomposing animal matter, and known as *ptomaines* (πτῶμα, a corpse) or *toxines*.

Choline is *hydroxyethyl-trimethyl ammonium hydroxide*, $N(C_2H_4OH)(CH_3)_3{\cdot}OH$, and can be artificially prepared by heating ethylene chlorhydrin with trimethylamine in aqueous solution. It is strongly alkaline and crystallises with difficulty: it is not poisonous, but when oxidised by nitric acid it yields *muscarine* or *hydroxycholine*, $N[C_2H_3(OH)_2](CH_3)_3{\cdot}OH$, which is a poisonous base found in the toad-stool, *Agaricus muscarius*.

When treated with hydriodic acid, choline yields the iodine derivative $N(C_2H_4I)(CH_3)_3{\cdot}I$, which with AgOH yields *neurine* or *trimethyl-vinyl ammonium hydroxide*, $N(C_2H_3)(CH_3)_3{\cdot}OH$. This is strongly alkaline and poisonous, but has not been crystallised; it is a product of the putrefaction of many kinds of animal matter.

Other ptomaines, beside neurine (from flesh) and muscarine (from fish), are *neuridine*, $C_5H_{14}N_2$ (from flesh), *gadinine*, $C_8H_{17}NO_2$ (from fish), *cadaverine*, or *pentamethylene diamine*, $C_5H_{16}N_2$, *putrescine* or *tetra-methylene diamine* $C_4H_{12}N_2$, *mydine*, $C_8H_{11}NO$, and *mydatoxine*, $C_8H_{13}NO_2$.

459. **Diamido-benzenes**, $C_6H_4(NH_2)_2$, or **phenylene diamines**, $N_2H_4(C_6H_4)''$, being disubstituted benzenes, exist in three forms, which are obtainable by the reduction of the corresponding dinitro-benzenes, or by distilling the three diamido-benzoic acids, $C_6H_3(NH_2)_2{\cdot}CO_2H$, with baryta. They are diacid bases. *Metaphenylene diamine* melts at 63° C. and boils at 287° C.; it is very soluble in water and gives a yellow colour with nitrous acid; it is used for the estimation of small quantities of nitrites. *Tri-*, *tetra-*, and *penta-amido-benzenes* are also known.

Diamido-naphthalenes, $C_{10}H_6(NH_2)_2$, or *naphthylene diamines*, corresponding with phenylene diamine, are obtained by the reduction of dinitronaphthalenes.

460. **Diamidodiphenyl**, or **benzidine**, $NH_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NH_2$, is produced by reducing the corresponding dinitro-derivative, obtained by direct nitration of diphenyl (p. 550); it is also formed by the intramolecular change of hydrazo-benzene (*q.v.*), a product of the reduction of azo-benzene, and is generally prepared on a large

scale from this source. It crystallises in colourless plates, melts at 122° C., dissolves in hot water, and sublimes. Its sulphate, $C_{12}H_8(NH_2)_2.H_2SO_4$, is very sparingly soluble. It is the parent substance of many important dyes. The two NH_2 groups occupy the para-positions with regard to the link between the phenyl groups.

Carbazole is *imidiphenyl*, $\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\!\!>\!NH$; it is formed by passing vapour of diphenylamine through a red-hot tube ($(C_6H_5)_2NH = (C_6H_4)_2NH + H_2$ (*cf.* diphenyl). It is also obtained at the end of the distillation of coal-tar, and as a secondary product in the preparation of aniline. It crystallises in plates (m.-p. 238° C.; b.-p. 351° C.), sublimes easily, and dissolves in alcohol and in ether.

Amides and Amic Acids.

461. **Amides are derived from NH_3, by the substitution of a negative** or acid radicle for hydrogen; thus, in acetamide, $CH_3C\begin{matrix}NH_2\\\diagup\!\!\diagdown\\O\end{matrix}$ the radicle acetyl, CH_3CO, has been substituted for one-third of the H in NH_3. The amides, like the amines (p. 638), may be primary, secondary, or tertiary, accordingly as one, two, or three atoms of H in the NH_3 group have been exchanged, and they may be monamides, diamides, or triamides, accordingly as they are formed upon the model of one, two, or three ammonia molecules.

Amides may be formed from ammonia in the same manner as amines, by the action of the chloride of an acid radicle, when the chlorine removes the ammonia-hydrogen, $CH_3CO{\cdot}Cl + 2NH_3 = CH_3CO{\cdot}NH_2 + NH_3HCl$ (*cf.* p. 660), or by the action of an ethereal salt, when the hydrogen is exchanged for the acid radicle, $CH_3CO{\cdot}OC_2H_5 + NH_3 = CH_3CO{\cdot}NH_2 + C_2H_5{\cdot}OH$. Amides may also be formed by dehydrating the ammonium salts of the acids, by heat or otherwise, when the ammonia-hydrogen and the OH group of the acid form water, leaving the NH_2 group in combination with the acid radicle, $CH_3CO{\cdot}ONH_4 = CH_3CO{\cdot}NH_2 + H_2O$. This mode of formation explains the characteristic property of the amides to be converted by hydrolysis into ammonia-salts, $CH_3CO{\cdot}NH_2 + H_2O = CH_3CO{\cdot}ONH_4$.

If primary or secondary amines be substituted for ammonia, or amine salts for ammonium salts, in the foregoing reactions, substituted amines, such as *ethylacetamide*, $CH_3CO{\cdot}NHC_2H_5$ and *acetanilide*, $CH_3CO{\cdot}NHC_6H_5$, are formed.

Nitrous acid converts the primary amides into the corresponding acids, $CH_3CO{\cdot}NH_2 + HO{\cdot}N : O = CH_3CO{\cdot}OH + N_2 + HOH$. Dehydrating agents convert them into nitriles (cyanides) of hydrocarbon radicles;

$$CH_3CO{\cdot}NH_2 = CH_3{\cdot}C \vdots N + H_2O.$$

The amides are distinctly basic, forming salts with acids, but far less so than the amines owing to the acid radicles. Indeed, the amidogen H has even an acid character, for it may be exchanged for metals.

Monamides.—*Formamide*, $HCO{\cdot}NH_2$, obtained by distilling ammonium formate, or by saturating ethyl formate with NH_3 and heating to 100°, for two days, in a sealed tube, is a liquid, boiling at 193° C., with decomposition—$2(HCO{\cdot}NH_2) = H_2O + CO + NH_3 + HCN$. Strong KOH converts it at once into potassium formate and NH_3.

Acetamide, $CH_3CO{\cdot}NH_2$, is prepared by the methods mentioned above. Instead of ammonium acetate, a mixture of NH_4Cl with dry sodium acetate may be used in

the third method. It crystallises in needles smelling of mice, fusing at 82° C. and boiling at 222° C., soluble in water and alcohol, but sparingly in ether. It is a weak base, forming unstable crystalline salts. Solution of acetamide dissolves silver oxide, and deposits *silver acetamide*, $C_2H_3O{\cdot}NHAg$. With mercuric oxide, crystals of *mercuric acetamide*, $(C_2H_3O{\cdot}NH)_2Hg$, are obtained. Boiling with water, especially in the presence of acids or alkalies, converts acetamide into acetic acid and ammonia. When distilled with powerful dehydrating agents, such as P_2O_5 or $ZnCl_2$, it yields *acetonitrile*, or *methyl cyanide*, $CH_3{\cdot}CN$.

The three chloracetic acids yield corresponding amides—*monochloracetamide*, $CH_2ClCO{\cdot}NH_2$; *dichloracetamide*, $CHCl_2CO{\cdot}NH_2$; and *trichloracetamide*, $CCl_3CO{\cdot}NH_2$, all crystalline solids with high boiling-points.

Acetanilide, $CH_3CO{\cdot}NH(C_6H_5)$ is prepared by boiling aniline with glacial acetic acid; it forms white prisms, soluble in hot water, melts at 112° C. and boils at 304° C. It is used as a febrifuge under the name of *antifebrine*. The *methyl-acetanilide*, $CH_3CO.NCH_3(C_6H_5)$, is a remedy for headaches; it is called *exalgin* and melts at 102° C.

Di-acetamide, $(CH_3CO)_2NH$, is obtained by heating acetamide in HCl gas: $2CH_3CO{\cdot}NH_2 + HCl = (CH_3CO)_2NH + NH_4Cl$; or by acting on acetamide with acetyl chloride; $CH_3CO{\cdot}NH_2 + CH_3CO{\cdot}Cl = (CH_3CO)_2NH + HCl$. It is a feeble acid and forms crystals soluble in water, melting at 77° C. and boiling at 223° C.

Tri-acetamide, $(C_2H_3O)_3N$ is obtained by heating acetonitrile with acetic anhydride to 200° C.; $CH_3CN + (C_2H_3O)_2O = (C_2H_3O)_3N$. It may be crystallised from ether, and is neither basic nor acid.

The amides of the higher fatty acids are formed when their glyceryl salts, such as palmitine, stearine, and oleine, are treated with strong ammonia.

Benzamide, $C_6H_5CO{\cdot}NH_2$, is precipitated when benzoyl chloride is treated with NH_3. It may be crystallised from hot water in plates, fuses at 130° C., and boils at 288° C. It is soluble in alcohol and ether, and resembles acetamide in its reactions; it forms a crystalline compound with HCl, and its aqueous solution dissolves mercuric oxide, *benzomercuramide*, $C_6H_5CO{\cdot}NHg$, being produced.

Glycolamide, $CH_2(OH)CO{\cdot}NH_2$, from ethyl glycolate and NH_3, crystallises in needles (m.-p. 120° C.), dissolves in water, and is easily converted by alkalies and acids into ammonia and glycollic acid. Glycolamide is also formed by heating glycolide in ammonia gas—$2NH_3 + (CH_2{\cdot}CO)_2O_2 = 2CH_2(OH)CO{\cdot}NH_2$.

Lactamide, $C_2H_4(OH)CO{\cdot}NH_2$, from NH_3 and ethyl lactate or lactide, forms crystals which fuse at 74° C. and volatilise unchanged.

462. **Sulphonamides** are amides from sulphonic acids, *e.g.*, $C_6H_5{\cdot}SO_2NH_2$, *benzene sulponamide*, and are prepared like the foregoing amides from the corresponding sulphonic acid derivatives. The compound $C_6H_4(CO_2H){\cdot}SO_2NH_2$, 1 : 2-*benzoic sulphonamide*, is of some importance as the parent substance of *saccharine*, the sugar-substitute made from toluene. Saccharine is 1 : 2-*benzoic sulpho-imide*, $C_6H_4\begin{<}^{CO}_{SO_2}\rangle NH$, also called benzoic sulphinide and 2-anhydro sulph-amine benzoic acid. By treating toluene with sulphuric acid it yields *o*- and *p*-toluenesulphonic acids, $C_6H_4(CH_3){\cdot}SO_2OH$; these are oxidised to the corresponding benzoic sulphonic acids, $C_6H_4(CO_2H){\cdot}SO_2OH$, which by treatment with PCl_5 become the dichlorides, $C_6H_4(COCl){\cdot}SO_2Cl$. Ammonia converts the 1 : 4-derivative into $C_6H_4(CONH_2){\cdot}SO_2NH_2$, which is insoluble in water, and the 1 : 2-derivative into $C_6H_4(CO_2NH_4){\cdot}SO_2NH_2$, which is soluble; when an acid is added to the solution of the latter, saccharine is precipitated. It is said to be 500 times sweeter than cane sugar; it melts at 224° C. It is sparingly soluble in water, but readily in alkalies since the H of the NH group is exchanged for metals to form soluble salts. The sodium salt is the commercial saccharine.

463. **Amidines.**—It is possible to represent the primary amides by two formulæ, $R{\cdot}C\begin{<}^{O}_{NH_2}$ and $R{\cdot}C\begin{<}^{OH}_{NH}$; the two amides corresponding with these formulæ do not, however, appear to exist, except in the case of glycolamide. Many derivatives of the amides exist in both forms; thus, the ethyl acetamide described above is $CH_3CO{\cdot}NHC_2H_5$, but the compound $CH_3C(NH){\cdot}OC_2H_5$ is also known, and is called *acetimidoether*. By acting on acetamide with PCl_5, *acetamido-chloride*, $CH_3CCl_2{\cdot}NH_2$, is obtained; but this readily loses HCl, and passes into *acetimido-chloride*,

$CH_3C(NH)\cdot Cl$, a derivative of the second general formula given above, Cl having been substituted for OH.

Amidines, $R\cdot C\begin{matrix}\diagup\!\!\!\diagup NH\\ \diagdown NH_2\end{matrix}$, may be regarded as derived from either formula, although the fact that they are obtained by treating the imido-chlorides with ammonia (or primary amines) seems to indicate that they are from the second formula : $R\cdot C(NH)\cdot Cl + NH_2R = R\cdot C(NH)\cdot NHR + HCl$. The *amidoximes* $R\begin{matrix}\diagup\!\!\!\diagup NOH\\ \diagdown NH_2\end{matrix}$ may be regarded as derived from the amidines ; they are the products of the action of hydroxylamines on the cyanides (nitriles) ; thus, hydrogen cyanide and hydroxylamine yield *isuret* (*methenyl-amidoxime*), isomeric with urea—

$$HCN + NH_2OH = HC(N\cdot OH)\cdot NH_2.$$

464. **Diamides.**—*Oxamide*, $CONH_2\cdot CONH_2$ is best prepared by shaking ethyl oxalate with solution of ammonia, when the mixture becomes hot and a white crystalline precipitate of oxamide separates ; $(COOC_2H_5)_2 + 2NH_3 = (CONH_2)_2 + 2(HO\cdot C_2H_5)$. If an alcoholic solution of ammonia be employed, or if ammonia gas be passed into ethyl oxalate, only half the ethoxyl (OC_2H_5) is exchanged for NH_2, and *ethyl oxamate* (*oxamethane*), $COOC_2H_5\cdot CONH_2$, is obtained. Oxamide is scarcely dissolved by water, alcohol, or ether, and is a perfectly neutral body. It may be crystallised in needles from a hot saturated solution of calcium chloride. When heated, a part sublimes unchanged. A red-hot tube decomposes the vapour, forming hydrocyanic acid and urea, $2(CONH_2)_2 = HCN + CO(NH_2)_2 + CO + CO_2 + NH_3$. By hydrolysis it yields oxalic acid and NH_3.

Oxamide is obtained by the distillation of ammonium oxalate, showing that the ammonium salt of a dibasic acid yields a di-amide. Since it contains the elements of cyanogen, it is not surprising to meet with oxamide in many reactions of cyanogen compounds ; it can be formed by mixing aqueous solutions of hydrocyanic acid and hydrogen di-oxide ; $2HCN + H_2O_2 = 2(CONH_2)_2$. The reaction of aldehyde with solution of cyanogen also produces oxamide ; and it is found among the products of the action of nitric acid on potassium ferrocyanide. The oxidation of potassium cyanide with manganese dioxide and dilute sulphuric acid also forms oxamide.

Dimethyl oxamide $(CONHCH_3)_2$, and *di-ethyl oxamide* $(CONHC_2H_5)_2$, are formed by the action of methylamine and ethylamine on ethyl oxalate. They crystallise from hot water. By acting on diethyl oxamide with PCl_5, a remarkable tertiary amine has been obtained, called *chloroxalethyline*, and having the formula $C_6H_9ClN_2$; it is an alkaline liquid, which boils at 217° C., and when acted on by hydriodic acid and red phosphorus, it yields, on distillation with soda, another liquid base, *oxalethyline*, $C_6H_{10}N_2$, which is poisonous, and produces the same symptoms as atropine, notably the dilatation of the pupil of the eye.

465. *Succinamide*, $C_2H_4(CONH_2)_2$, produced like oxamide, crystallises in sparingly soluble needles. At 200° C. it yields ammonia and *succinimide* ; $C_2H_4(CONH_2)_2 = NH_3 + C_2H_4(CO)_2NH$. This body is also formed when ammonium succinate is distilled. It is crystalline, and soluble in water and alcohol. By mixing the hot alcoholic solution with a little ammonia and silver nitrate, *silver succinimide*, $C_2H_4(CO)_2NAg$, is obtained in crystals.

The *imides*, which contain the group NH (imidogen), exhibit an acid character, allowing the H of this group to be exchanged for a metal.

466. **Carbamide, or urea,** $CO(NH_2)_2$, is the diamide of carbonic acid, $CO(OH)_2$, and is produced by heating NH_3 with ethyl carbonate at 180° C.—$CO(OC_2H_5)_2 + 2NH_3 = CO(NH_2)_2 + 2HOC_2H_5$; by treating NH_3 with carbonyl chloride (phosgene)—$COCl_2 + 4NH_3 = CO(NH_2)_2 + 2NH_4Cl$; by heating oxamide with mercuric oxide—$(CONH_2)_2 + HgO = CO(NH_2)_2 + Hg + CO_2$; or by heating a solution of CO in ammoniacal cuprous chloride—$CO + 2NH_3 + Cu_2Cl_2 = CO(NH_2)_2 + 2HCl + Cu$. But the best process for preparing it is to heat a solution of ammonium isocyanate, $NH_4\cdot NCO$, which is metameric with urea—$CO:N\cdot NH_4 = CO(NH_2)_2$. (See below.)

Urea is the chief form in which the nitrogen of the effete tissues is excreted from the human organism, and it is present in urine to the amount of about 1.4 per cent. by weight.

To extract it, the urine is filtered to separate mucus, evaporated to about an eighth of its bulk, cooled and mixed with about an equal volume of strong HNO_3, which must be quite colourless, showing it to be free from nitrous acid, which would decompose the urea: the latter is precipitated in pearly scales of urea nitrate, which is nearly insoluble in the acid, and sparingly soluble in water. This is collected on a filter, washed with ice-cold water till the washings are but slightly coloured, dissolved in boiling water, and mixed with precipitated $BaCO_3$, rubbed to a cream with water, as long as a fresh addition of the carbonate causes effervescence—

$$2(N_2H_4CO{\cdot}HNO_3) + BaCO_3 = CO_2 + 2N_2H_4CO + H_2O + Ba(NO_3)_2.$$

After filtering from the excess of $BaCO_3$, the liquid is evaporated on a steam-bath, when a mixture of urea and barium nitrate is obtained, from which the urea may be extracted by strong alcohol, and crystallised by evaporation.

Artificial urea. The preparation of urea without having resource to urine attracted much attention as one of the earliest examples of the artificial formation of an animal product from mineral sources. The original process (Liebig and Wöhler) was the following: 56 parts of well-dried potassium ferrocyanide, are mixed with 28 parts of dried manganese dioxide, the mixture heated to dull redness in an iron dish, and stirred until it ceases to smoulder. The cool residue is treated with cold water, filtered, and the solution (of potassium (iso)cyanate) decomposed with 41 parts of crystallised ammonium sulphate. It is then evaporated to dryness on a steam-bath, and treated with strong alcohol to extract the urea.

As a class experiment, a strong solution of potassium isocyanate may be mixed with an equal volume of a strong solution of ammonium sulphate, and divided into two parts, one of which is boiled for a minute, and cooled. If both portions be now stirred with strong (colourless) nitric acid, the first will simply effervesce violently, but the second will deposit abundant crystals of urea nitrate.

Urea crystallises in long prisms resembling nitre, which dissolve in an equal weight of cold water, and in five parts of cold alcohol; it is almost insoluble in ether. When heated, urea fuses at 132° C., and evolves much ammonia and some ammonium cyanate. If kept for some time at 150° C., the bulk of it is converted into *biuret*, produced from two molecules of urea by the loss of one molecule of ammonia; $2CO(NH_2)_2 = NH_3 + NH(CONH_2)_2$. When the temperature is raised to 170° C., the biuret again evolves ammonia, and is converted into cyanuric acid; $3NH(CONH_2)_2 = 3NH_3 + 2(CNOH)_3$.

Urea is not alkaline, but, like many amides, it is a weak base, and, though a diamide, forms salts like a monacid base; these are acid to litmus. The nitrate and oxalate are best known because they are sparingly soluble, and are obtained as crystalline precipitates when nitric and oxalic acids are stirred with solution of urea.

The nitrate, when heated, evolves a very pungent smell, and is decomposed with almost explosive violence at 150° C. *Urea oxalate* crystallises with 2Aq: $(N_2H_4CO)_2.H_2C_2O_4.2Aq$. *Urea hydrochloride*, $N_2H_4CO.HCl$, is formed, with evolution of heat, when HCl gas acts on dry urea; it solidifies to a crystalline deliquescent mass, which is decomposed by water.

Urea, like many other amides, forms compounds with the oxides of silver and mercury. The compound $N_2H_4CO.3Ag_2O$ is obtained as a grey crystalline powder when silver oxide is digested in solution of urea. When mercuric oxide is treated in the same way the compound $N_2H_4CO.HgO$ is formed; on adding mercuric

chloride to a solution of urea mixed with potash, a white precipitate of $2N_2H_4CO.3HgO$ is obtained, but if mercuric nitrate be employed, the precipitate is $N_2H_4CO.2HgO$. The formation of the last compound is the basis of Liebig's method for the determination of urea.

Urea also forms compounds with certain salts: the compound $N_2H_4CO.NaCl.Aq$. is obtained in crystals when urine is evaporated to a small bulk. When strong solutions of urea and $AgNO_3$ are mixed, crystals of $N_2H_4CO.AgNO_3$ are deposited. By mixing dilute solutions of urea and mercuric nitrate, a precipitate is formed having the formula $N_2H_4CO(HgO)_2HNO_3$.

By hydrolysis urea yields ammonia and carbonic acid, hence its transformation into ammonium carbonate when urine is allowed to putrefy.

Nitrous acid acts on urea, as on amides generally, converting the NH_2 into OH, and liberating N, but the $(HO)_2CO$ formed is at once decomposed into H_2O and CO_2: $(NH_2)_2CO + 2HNO_2 = N_4 + CO_2 + 3H_2O$. Hypochlorites and hypobromites (prepared by dissolving Br in alkalies) also expel all the nitrogen as gas—$(NH_2)_2CO + 3NaOBr + 2NaOH = N_2 + 3H_2O + Na_2CO_3 + 3NaBr$. This method is sometimes adopted for determining urea by measuring the nitrogen. The nitrogen is also liberated when urea is boiled with potash and a large excess of potassium permanganate, whereas, in most other amides, the bulk of the nitrogen is oxidised to nitric acid. When chlorine is passed into fused urea, hydrochloric acid and nitrogen are evolved, and the residue is a mixture of cyanuric acid with ammonium chloride—$3N_2H_4CO + Cl_3 = HCl + N + (CN)_3(HO)_3 + 2NH_4Cl$.

By boiling solution of urea with $AgNO_3$, a crystalline precipitate of silver isocyanate is obtained; $N_2H_4CO + AgNO_3 = NH_4NO_3 + AgNCO$.

Urea has been formed by passing NH_3 and CO_2 together through a red-hot tube; and by passing a mixture of benzene-vapour, ammonia and air over red-hot platinum wire.

Although most of the derivatives of urea behave as though they were derived from the formula $CO(NH_2)_2$, there are certain compounds which appear to be derivatives of a *pseudourea* of the form $NH{:}C(NH_2)(OH)$.

Biuret or *allophanamide*, $NH(CONH_2)_2$, is obtained by heating urea to 150° C. as long as it evolves NH_3 freely, extracting the residue with cold water, which leaves most of the cyanuric acid undissolved, precipitating the rest by lead acetate, removing the lead by H_2S, and evaporating the filtered solution, when the biuret crystallises with $1H_2O$. It is soluble in alcohol. Its alkaline aqueous solution gives a fine violet colour with $CuSO_4$. When heated in HCl gas, biuret is converted into guanidine hydrochloride; $NH(CONH_2)_2 + HCl = CO_2 + C(NH)(NH_2)_2.HCl$. Biuret is also obtained by heating ethyl allophanate with NH_3.

Allophanic acid has not been obtained; when liberated from its salts, it decomposes into CO_2 and urea; $NH_2CO{\cdot}NH{\cdot}COOH = CO(NH_2)_2 + CO_2$. *Ethyl allophanate* is formed when urea is acted on by ethyl chlorocarbonate (prepared by saturating alcohol with carbonyl chloride); $CO(NH_2)_2 + COCl{\cdot}OC_2H_5 = NH_2CO{\cdot}NH{\cdot}COOC_2H_5 + HCl$. It crystallises in prisms soluble in water and alcohol.

The hydrogen in urea, like that in other primary amides, may be exchanged for radicles, forming so-called *compound ureas*. Those containing positive radicles, such as *methyl carbamide*, $CO(NH_2)(NHCH_3)$, and *dimethyl carbamide*, $CO(NHCH_3)_2$, are derived from the isocyanates of the amines, just as urea is derived from ammonium isocyanate. Those containing acid radicles, such as *acetyl carbamide* or *acetyl urea*, $CO(NH_2)(NHC_2H_3O)$, obtained by the action of acetyl chloride upon urea, are called *ureides*. *Di-acetyl carbamide* is formed when acetamide is heated to 50° C. with $COCl_2$; $2NH_2C_2H_3O + COCl_2 = CO(NHC_2H_3O)_2 + 2HCl$.

The action of NH_3 on *bromacetylurea*, $NH_2{\cdot}CO{\cdot}NHCH_2BrCO$, produces *hydantoïn*, which is a reduction-product of alloxan (*q.v.*). The Br may be supposed to be exchanged for OH by the action of the ammonia solution, but hydantoïn appears to be an internal anhydride of the glycolylurea which would thus be formed, $NH_2{\cdot}CO{\cdot}NH{\cdot}CH_2OHCO$ giving $\underset{\text{———————}}{NHCO{\cdot}NH{\cdot}CH_2CO} + H_2O$.

Carbanilide, or *diphenyl urea*, $(NHC_6H_5)_2CO$, is prepared by heating urea with aniline; $(NH_2)_2CO + 2NH_2C_6H_5 = (NHC_6H_5)_2CO + 2NH_3$. It is slightly soluble in water, more soluble in alcohol, melts at 235° C. and boils at 260° C. Carbanilide is also formed when aniline is acted on by carbonyl chloride.

467. *Thiocarbamide* or *sulpho-urea*, $CS(NH_2)_2$, is the amide of thiocarbonic acid, $CS(OH)_2$. It is obtained from ammonium (iso)thiocyanate, $CS:N{\cdot}NH_4$, just as urea is obtained from the isocyanate. It crystallises easily from hot water, and

resembles urea in its chemical reactions; it melts at 169° C. PbO abstracts sulphur from it, converting it into cyanamide (*q.v.*). Its salts appear to be derived from the tautomeric form $NH:C(NH_2)(SH)$.

Thiocarbanilide, or *diphenyl sulphurea*, is formed when aniline is heated with carbon disulphide; $2NH_2C_6H_5 + CS_2 = CS(NHC_6H_5)_2 + H_2S$. It forms colourless crystals, insoluble in water, soluble in alcohol and ether, and melts at 154° C.

468. **Amic Acids.**—If only one of the acid hydroxyl groups of a dibasic acid is exchanged for NH_2 an amic acid, like *succinamic acid*, $C_2H_4(CONH_2)(COOH)$, is obtained. These acids are primary amides, and are generally obtained by heating the acid ammonium salts of the dibasic acids, just as the normal salts yield the diamides. Or the acid ethereal salts, like ethyl hydrogen oxalate, $COOH{\cdot}COOC_2H_5$, may be treated with NH_3.

Oxamic acid, $CONH_2{\cdot}COOH$, is prepared by heating ammonium hydrogen oxalate till it begins to give off CO_2 (see above). A mixture of oxamide and oxamic acid is left, from which water extracts the acid. Ammonium oxamate is formed when oxamide is boiled with solution of ammonia; $(CONH_2)_2 + H_2O = CONH_2{\cdot}COONH_4$. On adding HCl, the oxamic acid is obtained as a crystalline precipitate, sparingly soluble in water, alcohol, and ether, and converted into hydrogen ammonium oxalate by boiling with water. It fuses at 210° C., and decomposes, yielding oxamide, formic acid, and water. Treated with PCl_5, it yields *oximide* $(CO_2):NH$, a soluble neutral substance.

469. **Carbamic acid**, $CO(NH_2)OH$, has not been obtained in the free state, but *ammonium carbamate* is formed when ammonia combines with CO_2; $2NH_3 + CO_2 = CO(NH_2)(ONH_4)$. The ammonium salt is best prepared by saturating absolute alcohol with dry ammonia gas, and passing dry CO_2 into the solution, when the ammonium carbamate crystallises. It is soluble in water, and is converted into ammonium carbonate by boiling the solution; $CO(NH_2){\cdot}ONH_4 + H_2O = CO(ONH_4)_2$. Ammonium carbamate sublimes and dissociates below 100° C., and when heated, in a sealed tube, to 135° C., yields urea and ammonium carbonate; $2CO(NH_2){\cdot}ONH_4 = CO(NH_2)_2 + CO(ONH_4)_2$.

When ammonium carbonate is distilled, part of it is converted into the carbamate; $CO(ONH_4)_2 = CO{\cdot}NH_2(ONH_4) + H_2O$. This accounts for the presence of ammonium carbamate in the commercial carbonate (p. 355).

Ethyl carbamate, or *urethane*, $CO(NH_2)OC_2H_5$, is formed by the action of solution of ammonia upon ethyl carbonate at 100° C.—

$$CO(OC_2H_5)_2 + NH_3 = CO(NH_2)OC_2H_5 + HO{\cdot}C_2H_5.$$

It forms tabular crystals, soluble in water, alcohol, and ether, melts at 50° C., and boils at 184° C. Boiled with potash, it yields the carbonate, alcohol, and ammonia: $CO(NH_2)OC_2H_5 + 2KOH = CO(OK)_2 + NH_3 + HO{\cdot}C_2H_5$. Heated with ammonia, it gives alcohol and urea: $CO(NH_2)OC_2H_5 + NH_3 = CO(NH_2)_2 + HO{\cdot}C_2H_5$.

Thiocarbamic acid, $CS(NH_2)SH$, is obtained as an ammonium salt by acting on carbon bisulphide with ammonia in alcoholic solution: $2NH_3 + CS_2 = CS(NH_2)SNH_4$, the reaction corresponding with that between NH_3 and CO_2. The ammonium thiocarbamate crystallises in yellow prisms. When decomposed by HCl, it yields thiocarbamic acid as a yellow unstable crystalline body, which decomposes spontaneously: $CS(NH_2)SH = H_2S + HSCN$ (thiocyanic acid).

470. **Guanidines.**—These compounds, which are of much importance on account of their physiological significance, are amidines (p. 668) of carbonic acid. Guanidine itself, the parent substance, is also called *imido-urea*, since it may be regarded as containing an imodo-group in the place of the oxygen of urea; thus, $CO(NH_2)_2$, urea; $C(NH)(NH_2)_2$, guanidine. The guanidines can be prepared synthetically by heating

the hydrochloride of an amine with cyanamide dissolved in alcohol—*e.g.*, $CN{\cdot}NH_2 + NH_3,HCl = C(NH)(NH_2)_2,HCl$.

Guanidine, or *carbon-diamide-imide*, $C(NH)(NH_2)_2$, occurs in vetch seeds and sugar beet. It was so called because originally obtained by the oxidising action of $KClO_3$ and HCl on *guanine*, a feeble base extracted from guano. It is prepared by heating ammonium thiocyanate in a retort at 190° C. for several hours. A portion of the thiocyanate becomes thiocarbamide, which then reacts with the remaining ammonium thiocyanate yielding guanidine thiocyanate; $CS(NH_2)_2 + NH_3,CNSH = C(NH)(NH_2)_2,CNSH + H_2S$. This is dissolved in a little water mixed with half its weight of potassium carbonate, and evaporated to dryness, when a mixture of guanidine carbonate and potassium thiocyanate is obtained. This is boiled with alcohol, which dissolves the thiocyanate, and leaves *guanidine carbonate* $(N_3H_5C)_2.H_2CO_3$, which may be recrystallised from water. This is converted into *guanidine sulphate*, $(N_3H_5C)_2.H_2SO_4$, and decomposed by baryta-water; the filtrate from the $BaSO_4$ is evaporated over sulphuric acid, when guanidine is obtained as a deliquescent crystalline substance, which is strongly alkaline, and absorbs CO_2 from the air. It is a strong monacid base, and yields well-crystallised salts.

Guanidine nitrate, $N_3H_5C.HNO_3$, like urea nitrate, is sparingly soluble in water, and crystallises in plates. Guanidine is soluble in alcohol. Its platinum salt, $(N_3H_5C.HCl)_2PtCl_4$, is sparingly dissolved by absolute alcohol. When hydrolysed with baryta-water, guanidine yields urea and ammonia; $C(NH_2)_2NH + H_2O = (NH_2)_2CO + NH_3$. Heated with strong potash, it gives potassium carbonate and ammonia; $C(NH_2)_2(NH)'' + 2KOH + H_2O = C(OK)_2O + 3NH_3$. Hot dilute H_2SO_4 converts it into NH_3 and urea, which combine with the acid.

Guanidine hydriodide is obtained when cyanogen iodide is heated with alcoholic ammonia in a sealed tube at 100° C.;

$$I{\cdot}CN + 2NH_3 = C(NH)(NH_2)_2.HI.$$

Nitroguanidine, $C(NH)(NH_2)(NHNO_2)$, is obtained by nitrating guanidine, and yields *amidoguanidine*, $C(NH)(NH_2)(NHNH_2)$, when reduced. This compound is of interest as yielding hydrazine, NH_2 and CO_2, when hydrolysed. Hydrazoic acid (p. 107) may also be obtained from it by first treating it with nitrous acid to form *diazo-guanidine*, $C(NH)(NH_2)(NHN : N{\cdot}OH)$, and hydrolysing this.

Diphenyl guanidine, or *melaniline*, $C(NH{\cdot}C_6H_5)_2NH$, is a crystalline base produced by the action of cyanogen chloride on aniline—

$$Cl{\cdot}CN + 2NH_2C_6H_5 = C(NH{\cdot}C_6H_5)_2NH.HCl.$$

Amido-Acids.

471. These may be prepared from the chloro-substituted acids by treatment with ammonia; thus amido-acetic acid results from the action of ammonia on monochloracetic acid, $CH_2Cl{\cdot}CO_2H + 2NH_3 = CH_2(NH_2){\cdot}CO_2H + NH_3.HCl$; also by the reduction of the nitro-acids or the cyano-acids by nascent hydrogen—

$$CH_2(NO_2){\cdot}CO_2H + H_6 = CH_2(NH_2){\cdot}CO_2H + 2H_2O.$$
$$CH_2(CN){\cdot}COOH + H_4 = CH_2{\cdot}CH_2(NH_2){\cdot}COOH.$$

In the aromatic group the nitro-acids are reduced to obtain the amido-acids. They are metameric with the amides of hydroxy-acids, but are distinguished by their greater stability towards hydrolysing agents, the amido-group being more firmly held and less easily evolved as NH_3. Like other ammonia derivatives they may be primary, secondary, or tertiary, as $NH_2(CH_2COOH)$, $NH(CH_2COOH)_2$, $N(CH_2COOH)_3$, obtained from the mono- di- and tri-chloracetic acids respectively. The

open-chain derivatives may be α-, β-, or γ-amido-acids, like other open-chain substituted acids.*

By action of nitrous acid the NH_2 group is converted into an OH group, as in the case of the amines and amides, a hydroxy-acid being produced—$CH_2(NH_2)\cdot CO_2H + NO\cdot OH = CH_2(OH)\cdot CO_2H + N_2 + HOH$. But there is a tendency for the amido-acids to undergo the diazo-reaction (p. 106).

When heated with baryta the amido-acids lose CO_2 and give the corresponding amines – $CH_2NH_2\cdot COOH = CH_3NH_2 + CO_2$.

Just as the α-hydroxy-acids form lactides by loss of water from both the COOH and the OH groups (p. 603), so the amido-acids are converted by dehydrating agents into anhydrides by loss of water from the NH_2 and COOH groups; thus two mols. glycocoll, $CH_2NH_2\cdot COOH$, yield $NH\langle^{CO\cdot CH_2}_{CH_2\cdot CO}\rangle NH$. Further, the γ- and δ-amido-acids yield internal anhydrides, *lactams*, corresponding with the lactones (p. 607); *γ-amidobutyric acid*, $CH_2NH_2\cdot CH_2\cdot CH_2\cdot COOH$, yields *γ-butyrolactam*, $CH_2\underline{NH\cdot CH_2\cdot CH_2}CO$.

472. *Amidoformic acid*, $NH_2\cdot CO_2H$, is identical with carbamic acid.

Glycocoll, *glycocine*, or *glycine*, is *amido-acetic acid*, $CH_2(NH_2)CO_2H$, and is prepared by heating hippuric acid (benzoyl amido-acetic) for half an hour with 4 parts of strong HCl, which converts it into benzoic acid and glycocine hydrochloride—

$$\underset{\textit{Hippuric acid.}}{CH_2(NHC_6H_5CO)\cdot CO_2H} + HCl + H_2O = \underset{\textit{Benzoic acid.}}{C_6H_5CO_2H} + \underset{\textit{Glycocine hydrochloride.}}{CH_2(NH_2)CO_2H.HCl}.$$

The solution is mixed with water and cooled, when most of the benzoic acid crystallises out; the filtrate is evaporated to dryness on a steam-bath, the glycocine hydrochloride extracted by water, boiled with lead hydroxide, filtered from the lead oxychloride, the dissolved lead precipitated by H_2S, and the filtrate evaporated. when it deposits the glycocine in transparent rhombic prisms, easily soluble in water, sparingly in alcohol, and insoluble in ether.

Glycocoll has a sweet taste, fuses at 232° C., evolving ammonia and methylamine. Its solution gives a red colour with Fe_2Cl_6, and a blue with $CuSO_4$; if this blue solution be mixed with potash and alcohol, it deposits blue needles of the formula $(NH_2\cdot CH_2\cdot CO_2)_2Cu.Aq$. A sparingly soluble silver salt, $NH_2\cdot CH_2CO_2Ag$, may also be obtained, but these compounds do not behave like ordinary salts of the metals (*cf.* synthesis of hippuric acid). Like other amido-acids, glycocine plays the part of a base and an acid. It forms hydrochlorides containing, respectively, one and two molecules of glycocine, and the latter forms a crystalline platinum salt. Crystalline compounds of glycocine with salts are also known.

From the behaviour of the metallic and other derivatives of glycocoll, it appears probable that the constitution of this (and of other) amido-acids is not that represented, but partakes of the nature of an intramolecular ammonia salt—$CH_2\langle^{NH_2}_{CO}\rangle O$.

Glycocoll can also be prepared by heating bromacetic acid with ammonia, and by passing cyanogen into a boiling saturated aqueous solution of hydriodic acid—

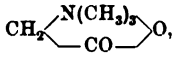
$$C_2N_2 + 2H_2O + 5HI = CH_2(NH_2)\cdot CO_2H + NH_4I + I_4.$$

* The prefixes *amino-*, *imino-*, *anilino-*, &c., are now often substituted for amido-, imido-, anilido-, &c.

Both methods afford a means of synthesising glycocol, which derives its name from the fact that it may be obtained by boiling glue (or gelatine) with dilute sulphuric acid (*sugar of gelatine ; γλυκυς, sweet ; κολλα, glue.*)

Sarcosine, or *methyl glycocoll*, $CH_2(NHCH_3)\cdot CO_2H$, may be obtained by heating bromacetic acid with methylamine (in place of ammonia, which yields glycocine). It is also formed when the creatine extracted from flesh is boiled with baryta. Caffeine yields it under similar treatment. Sarcosine forms prismatic crystals, very soluble in water and of sweet taste. It is sparingly soluble in alcohol, insoluble in ether, and may be sublimed. Its reaction is neutral, but it combines with acids and bases.

Betaine, or *tri-methyl-glycocoll*, $CH_2[N(CH_3)_2]\cdot CO_2CH_3$, or more probably—



is found in the juice of beet-root (*Beta vulgaris*), and may be formed synthetically by the action of trimethylamine on chloracetic acid—

$$CH_2Cl\cdot CO_2H + N(CH_3)_3 = CH_2[N(CH_3)_2]\cdot CO_2CH_3 + HCl.$$

Betaine hydrochloride is also obtained by the careful oxidation of choline hydrochloride—

$$N(C_2H_4OH)(CH_3)_3\cdot Cl + O_2 = CH_2[N(CH_3)_2]\cdot CO_2CH_3,HCl. + H_2O.$$

Betaine is soluble in water and alcohol, and forms salts with the acids.

Anilido-acetic acid or **phenylglycocine**, $CH_2(NHC_6H_5)\cdot COOH$, prepared from bromacetic acid and aniline, melts at 127° C. It is important as the parent substance of artificial indigo.

Acetylglycocine, or *aceturic acid*, $CH_2(NHCH_3CO)\cdot COOH$, from acetyl chloride and silver glycocine, melts at 206° C.

473. **Hippuric acid**, or *benzoylglycocoll*, or *benzamidoacetic acid*, $CH_2(NHC_6H_5CO)\cdot CO_2H$, is prepared from the urine of horses or cows (preferably the latter) by evaporating it to about an eighth of its bulk and adding an excess of HCl. On standing, long prisms of hippuric acid are deposited, which may be decolorised by dissolving in boiling water and adding a little chlorine-water, when the colourless acid will crystallise out on cooling. If the animal has undergone much exercise, or the urine has decomposed, benzoic acid is obtained instead of hippuric, and if a dose of benzoic acid is taken, it is found as hippuric acid in human urine, which contains naturally but a minute proportion.

It may be synthesised by heating benzoyl chloride with silver glycocoll (*cf.* salts of glycocoll, p. 674).

$$CH_2(NH_2)\cdot CO_2Ag + C_6H_5COCl = CH_2(NHC_6H_5CO)\cdot CO_2H + AgCl;$$

or benzamide with chloracetic acid—

$$CH_2Cl\cdot CO_2H + C_6H_5CO\cdot NH_2 = CH_2(NHC_6H_5CO)\cdot CO_2H + HCl.$$

Hippuric acid crystallises in rhombic prisms, sparingly soluble in cold water, soluble in hot water and in alcohol, but insoluble in ether, which distinguishes it from benzoic acid. Like benzoic, it dissolves easily in ammonia, and is precipitated, in feathery crystals, by hydrochloric acid; but these are not dissolved on adding ether.

The more complex character of hippuric acid is shown by the action of heat; for, whereas benzoic acid sublimes without decomposition, hippuric assumes a red colour, gives a small sublimate of benzoic acid and evolves hydrocyanic acid, *benzamide*, $C_6H_5CO\cdot NH_2$, and *benzonitrile*, or *phenyl cyanide*, $C_6H_5\cdot CN$, which smells of bitter almonds.

The *hippurates* resemble the benzoates; in solution, they give a buff precipitate with ferric chloride.

474. Glycocoll may be regarded as the parent substance of two physiologically important compounds, ***creatine*** and ***creatinine***.

When solutions of cyanamide and glycocoll are mixed, *glycocyamine*, or *guanidoacetic acid*, $CH_2[C(:NH)(NH_2)(NH)]\cdot CO_2H$, is formed. If glycocoll be regarded as an amine, $NH_2(CH_2\cdot CO_2H)$, then the formation of glycocyamine is only in accord with the general method for producing guanidines (p. 672). When glycocyamine hydrochloride is heated at 160° C. it becomes *glycocyamidine* hydrochloride by loss of water—

$$NH{:}C\begin{cases}NH_2\\ NH\cdot CH_2\cdot CO_2H\end{cases} = NH{:}C\begin{cases}NHCO\\ \cdot\\ NHCH_2\end{cases} + H_2O.$$

Creatine and creatinine are methylglycocyamine and methylglycocyamidine respectively.

Creatine, or *methylglycocyamine* (*κρέας*, *flesh*), $C_4H_9N_3O_2$, or $NH:C\begin{cases}NH_2\\ N(CH_3)\cdot CH_2\cdot CO_2H\end{cases}$, is obtained from chopped flesh by soaking it in cold water, squeezing it in a cloth, heating the liquid till the albumin coagulates, straining, adding baryta to precipitate phosphoric acid, and evaporating the filtrate to a syrup on the steam-bath; on standing for some hours the creatine crystallises out.

It may also be prepared from Liebig's extract of meat by dissolving it in 20 parts of water, adding tribasic lead acetate, filtering, removing the excess of lead by H_2S, and evaporating to crystallisation. Granular crystals of creatine are sometimes met with in Liebig's extract. The flesh of fowls yields 0.32 per cent. of creatine, that of cod-fish 0.17, beef 0.07 per cent.

Creatine forms prismatic crystals (with $1H_2O$) easily soluble in hot water, but very sparingly in alcohol and ether. It is neutral in reaction, but behaves as a feeble monacid base. *Creatine nitrate*, $C_4H_9N_3O_2.HNO_3$, crystallises in prisms. When the solutions of its salts are heated above 30° C., they are converted into salts of creatinine, a stronger base containing H_2 and O less than creatine. When boiled with baryta water, creatine is hydrolysed to sarcosine and urea—

$$CH_2[C(:NH)(NH_2)(NCH_3)]\cdot CO_2H + H_2O = CO(NH_2)_2 + CH_2NH(CH_3)\cdot CO_2H.$$

Creatine has been prepared synthetically by heating cyanamide with an alcoholic solution of sarcosine or methyl glycocoll, thus settling its constitution. When it is warmed with solution of sodium hypobromite, two-thirds of its nitrogen is liberated. By heating creatine in aqueous solution with mercuric oxide, it is converted into oxalic acid and *methyl-guanidine*, $C(NH)(NH_2)(NHCH_3)$.

Creatinine, or *methylglycocyamidine*, $C_4H_7N_3O$, or $NH:C\begin{cases}NH\text{——}CO\\ \cdot\\ N(CH_3)\cdot CH_2\end{cases}$, is prepared by heating creatine in a water-bath and passing a current of pure HCl over it as long as any water is formed. The hydrochloride thus obtained is dissolved in water, decomposed by lead hydroxide, the solution filtered and slowly evaporated, when it deposits prismatic crystals of $C_4H_7N_3O.2Aq$, which lose water on exposure to air, becoming opaque. If it be dissolved in cold water, and evaporated *in vacuo*, the original hydrated crystals are reproduced, but if it be dissolved in boiling water and the solution evaporated, it deposits tabular crystals which contain no water. The solution of these crystals when kept for some time at 60° C. deposits the prismatic hydrated creatinine.

Creatinine is much more soluble in water than creatine is, requiring about 12 parts of cold water. It dissolves in about 100 parts of cold alcohol. It has an alkaline reaction, and is a strong monacid base. It

is characterised by forming a sparingly soluble crystalline compound with zinc chloride, $(C_4H_7N_3O)_2ZnCl_2$. In contact with water, especially in presence of bases, creatinine is converted into creatine by hydration.

When creatinine is boiled with baryta-water, it yields ammonia and *methyl-hydantoin*, $\begin{matrix}NHCO\cdot N(CH_3)\cdot CH_2\\ \vert\quad\quad\quad\quad\vert\\ \quad\quad CO\end{matrix}$.

Creatinine does not appear to exist as such in flesh, though it is easily produced from it by the dehydration of the creatine. A substance having the same composition as creatinine exists in considerable quantity in urine (about two grams in the urine of twenty-four hours), but its properties are not quite the same as those of the creatinine prepared from the creatine of flesh. In order to prepare urinary creatinine, the urine is mixed with one-twentieth of its volume of a cold saturated solution of sodium acetate, and with one-fourth of its volume of a cold saturated solution of mercuric chloride; this produces an amorphous precipitate which is quickly filtered off, and the filtrate is set aside for forty-eight hours, when it deposits a granular precipitate, appearing in spheres under the microscope. This precipitate is suspended in cold water, and decomposed by H_2S, the mercuric sulphide is filtered off, and the acid filtrate evaporated over sulphuric acid, when it leaves crystals of the hydrochloride, $C_4H_7N_3O.HCl$. The concentrated aqueous solution of this salt is decomposed, in the cold, with lead hydrate, when an alkaline filtrate is obtained, which has a bitter taste, and, by spontaneous evaporation, yields prismatic crystals of $C_4H_7N_3O.2H_2O$, which rapidly become opaque and anhydrous when exposed to air. If heat be employed during the preparation of the body, tabular crystals of $C_4H_7N_3O$ are obtained, which are unchanged by exposure to air. The urinary creatinine requires 362 parts of cold alcohol to dissolve it, while flesh-creatinine requires only 102 parts. It is a more powerful reducing-agent than creatinine prepared from flesh-creatine.

475. Propionic acid can give rise to two substituted acids (*cf.* p. 580), consequently there are two *amido-propionic acids*. The α-acid is called *alanine*,

$$CH_3\cdot CH(NH_2)\cdot CO_2H,$$

prepared by the action of ammonia on α-chloropropionic acid. It dissolves in water and becomes ethylidene lactic acid when treated with nitrous acid.

Butalanine, which occurs in the pancreas of the ox is *α-amido-isovaleric acid*,

$$(CH_3)_2 : CH\cdot CH(NH_2)\cdot CO_2H.$$

476. **Leucine**, or *α-amido-caproic acid*, $CH_3\cdot[CH_2]_3\cdot CH(NH_2)\cdot CO_2H$, is prepared by boiling horn shavings (one part) with sulphuric acid ($2\frac{1}{2}$ parts) and water ($6\frac{1}{2}$ parts) in a reflux apparatus, for twenty-four hours. The hot liquid is neutralised by lime, filtered, and evaporated to about one-third; it is then carefully neutralised with H_2SO_4 and evaporated till crystals of leucine and tyrosine are deposited on cooling; by recrystallisation from water the tyrosine crystallises first.

Several other animal substances yield leucine and tyrosine when boiled with dilute sulphuric acid, or fused with potash. The *elastine* composing the cervical ligament of the ox yields more than horn. Leucine also occurs extensively in animals and vegetables. It is found in the liver, spleen, lungs, and pancreas; also in caterpillars and spiders; in the white sprouts of vetch, in yeast, and in putrefying cheese.

Leucine crystallises in pearly scales, moderately soluble in water, slightly in alcohol, and insoluble in ether. It fuses at 170° C., and may be partly sublimed, though much of it decomposes, yielding amylamine; $C_5H_{10}(NH_2)\cdot CO_2H = NH_2\cdot C_5H_{11} + CO_2$. Its reaction is neutral, but it forms compounds both with acids and bases. Hydriodic acid converts it into caproic acid and ammonia—

$$C_5H_{10}(NH_2)\cdot CO_2H + 2HI = C_5H_{11}\cdot CO_2H + NH_3 + I_2.$$

With nitrous acid it yields *leucic* or *hydroxy-caproic* acid—

$$C_5H_{10}(NH_2)\cdot CO_2H + HNO_2 = C_5H_{10}(OH)\cdot CO_2H + N_2 + H_2O.$$

Leucine is obtained synthetically from ammonia and bromocaproic acid ; $NH_3 + C_5H_{10}Br{\cdot}CO_2H = C_5H_{10}(NH_2){\cdot}CO_2H + HBr$; also by the reaction between valeraldehyde-ammonia, HCN, HCl and H_2O.

$$C_5H_{10}O{\cdot}NH_3 + HCN + HCl + H_2O = C_5H_{10}(NH_2){\cdot}CO_2H + NH_3HCl.$$

The leucine from plants appears to differ from that from animals, being optically active and existing in the usual three modifications (p. 604).

Tyrosine (*τυρός, cheese*) or *4-hydroxy-phenyl-amido-propionic acid*—

$$CH_2(C_6H_4OH){\cdot}CH(NH_2){\cdot}CO_2H,$$

is obtained, together with leucine, when albuminoid or gelatinoid bodies are boiled with dilute sulphuric acid or fused with potash. It crystallises in needles, which are sparingly soluble, even in hot water, sparingly soluble in alcohol, and insoluble in ether. It melts at 235° C., and is lævo-rotatory. Like leucine, it behaves both as a feeble acid and a feeble base. When its aqueous solution is boiled with mercuric nitrate it gives a yellow precipitate, which becomes red when boiled with nitric acid containing nitrous acid. With chlorine, it yields chloranil, $C_6Cl_4O_2$, and with fused potash, NH_3, and potassium parahydroxy-benzoate and acetate;

$$C_6H_4OH{\cdot}C_2H_3NH_2{\cdot}CO_2H + 2KOH = NH_3 + C_6H_4OH{\cdot}CO_2K + CH_3{\cdot}CO_2K + H_2.$$

477. *Amido-succinamic acid*, $CH_2CONH_2{\cdot}CHNH_2CO_2H$, or **asparagine**, is found in the shoots of asparagus and of other plants grown in the dark. It is of very frequent occurrence in plants, being found in marsh-mallow, vetches, peas, beans, mangold-wurzel, lettuces, potatoes, chestnuts, and dahlia roots. It may be extracted from the expressed juices of the plants by boiling to coagulate the albumin, filtering, and evaporating to a syrup, when the asparagine crystallises, on standing, in rhombic prisms (with $1H_2O$) which may be recrystallised from boiling water. It is nearly insoluble in alcohol and ether. It behaves as a weak acid and a weak base. By ferments, asparagine is converted into ammonium succinate ; by nitrous acid into malic acid—

$$C_2H_3NH_2(CO{\cdot}NH_2)(CO{\cdot}OH) + 2HNO_2 = C_2H_3OH(CO{\cdot}OH)(CO{\cdot}OH) + N_4 + 2H_2O.$$

From this reaction it was formally inferred that asparagine was the amide of malic acid, with which, however, it is only isomeric. Ordinary asparagine is lævo-rotatory ; the dextro-form has been found in the mother-liquor from crude asparagine, and is much sweeter than ordinary asparagine. A solution of the two in equal proportions is inactive, but the asparagines are deposited from it in crystals, which are, respectively, right- and left-handed. The isomeric derivatives from each kind retain the optical properties of their source. When asparagine is boiled with acids or alkalies, it is converted into *l-amidosuccinic* or *aspartic acid*—

$$C_2H_3NH_2(CO{\cdot}NH_2)(CO{\cdot}OH) + H_2O = C_2H_3NH_2(CO{\cdot}OH)(CO{\cdot}OH) + NH_3.$$

Aspartic acid is sparingly soluble in cold water and alcohol, but may be crystallised from hot water. Nitrous acid substitutes OH for the NH_2 in aspartic acid, converting it into malic acid. Aspartic acid is found in the molasses from beet-root juice, and occurs among the products of the action of sulphuric acid and of zinc chloride upon albuminous substances.

478. *Amidobenzoic acids*, $C_6H_4(NH_2){\cdot}CO_2H$. Of these the 1 : 2-acid or **anthranilic acid** is of importance, being an oxidation product of indigo. It is prepared by reducing 1 : 2-nitrobenzoic acid ; it sublimes in needles, melts at 145° C. and dissolves in hot water ; the solution tastes sweet and fluoresces blue.

Methyl anthranilate (m.-p. 25°·5 C.) in dilute solution smells of orange-blossom oil (*neroli oil*), of which it is a constituent.

The internal anhydride or lactam, *anthranil*, $C_6H_4\begin{smallmatrix}CO\\NH\end{smallmatrix}\rangle$, might be expected to be formed by dehydration of anthranilic acid, this being a 1 : 2-derivative (*cf.* p. 674); it cannot be so obtained, however, but is a product of the reduction of 1 : 2-nitrobenzaldehyde. It dissolves in alkalies to form salts of anthranilic acid. By

treating it, or anthranilic acid, with $COCl_2$, *isatoic anhydride*, $C_6H_4\langle{}^{CO\cdot O}_{NH\cdot CO}$, an oxidation-product of indigo, is obtained.

Amidophenylacetic acids, $C_6H_4(NH_2)\cdot CH_2CO_2H$, are obtained by reducing the corresponding nitro-acids, but only the *m*- and *p*- acids are known in the free state; attempts to prepare the 1 : 2-acid produce *oxindol*, $C_6H_4\langle{}^{CH_2}_{NH}\rangle CO$, which is an internal anhydride or lactam of the acid (p. 674). The same happens in the case of 1 : 2-*amidophenylglyoxylic acid* or *isatic acid*, $C_6H_4(NH_2)\cdot CO\cdot CO_2H$, a ketonic acid; in this case the anhydride is a *lactim*, *isatin*, $C_6H_4\langle{}^{CO}_{N}\rangle C\cdot OH$.

These compounds are closely related to indigo and will receive further attention in connection with that substance.

479. **Amidosulphonic Acids.**—*Taurine, amido-ethyl-sulphonic acid*, or *amido-isethionic acid*, $C_2H_4(NH_2)SO_3H$, is a decomposition-product of taurocholic acid (*q.v.*) and is prepared by boiling ox-gall with dilute HCl, evaporating to dryness on the steam-bath, and treating the residue with absolute alcohol, which leaves the taurine undissolved. This is dissolved in water, from which it crystallises in large four-sided prisms sparingly soluble in cold water, and insoluble in alcohol and ether. It fuses at 240° C. and is decomposed. It has no acid reaction, but it forms salts with bases. When fused with KOH, it yields the acetate and sulphite of potassium—

$$C_2H_4(NH_2)\cdot SO_3H + 3KOH = CH_3\cdot COOK + K_2SO_3 + NH_3 + H_2O + H_2.$$

Nitrous acid substitutes OH for the NH_2, producing isethionic acid.

Synthesis of taurine:—C_2H_4 is absorbed by SO_3, the product dissolved in water, neutralised with NH_3, and evaporated to crystallisation; $C_2H_4 + SO_3 + H_2O + NH_3 = C_2H_4OH\cdot SO_3NH_4$ (*ammonium isethionate*). When this is heated to 220° C., it yields taurine—$C_2H_4OH\cdot SO_3NH_4 = C_2H_4NH_2.SO_3H + H_2O$.

Taurine may also be synthesised by converting ethene into glycol-chlorhydrin, $HO\cdot C_2H_4\cdot Cl$, heating this with K_2SO_3 to obtain *potassium isethionate*—

$$HO\cdot C_2H_4\cdot Cl + K_2SO_3 = HO\cdot C_2H_4\cdot SO_3K + KCl;$$

distilling the isethionate with phosphoric chloride—

$$HO\cdot C_2H_4\cdot SO_3K + PCl_5 = PO_2Cl + HCl + KCl + Cl\cdot C_2H_4\cdot SO_2Cl$$ (*isethionic chloride*);

heating this with water—

$$Cl\cdot C_2H_4\cdot SO_2Cl + HOH = HCl + Cl\cdot C_2H_4\cdot SO_2\cdot OH$$ (*chlor-ethylsulphonic acid*);

and heating this to 100° C. with ammonia in a sealed tube—

$$Cl\cdot C_2H_4\cdot SO_2\cdot OH + 2NH_3 = NH_3HCl + NH_2\cdot C_2H_4\cdot SO_2\cdot OH$$ (*taurine*).

Some taurine exists as such in the bile; it has been found in the kidneys, lungs, and muscles. When solution of taurine is evaporated with potassium cyanate, it yields *potassium tauro-carbamate*, $NH_2CONH\cdot CH_2\cdot CH_2SO_3K$; tauro-carbamic acid is found in the urine when taurine is taken internally; it forms crystals easily soluble in water.

Amidobenzenesulphonic acid (see p. 664).

Diazo- and Azo-Compounds.

480. **Diazo-Compounds.**—It has been already noticed that the amines of open-chain hydrocarbons show no tendency to undergo the *diazo-reaction* described on p. 106, whereas the amines of closed-chain hydrocarbons readily do so at low temperatures. It thus happens that *diazo-compounds* of the type $R\cdot N : N\cdot X$, where R is a positive and X a

negative radicle, are only known when R is a radicle containing a benzene ring.

There is, however, a tendency for the amido-acids of the open-chain series to undergo the diazo-reaction, although the *diazo-acids* produced appear to be differently constructed from the true diazo-compounds, and have only been isolated as ethereal salts or as amides.

Diazoacetic acid, $\overset{\cdot\cdot}{\underset{N}{\overset{N}{\rangle}}}CH\cdot CO_2H$, has not been isolated, but *ethyl diazoacetate*, $N_2CH\cdot CO_2C_2H_5$, is precipitated as a yellow oil when the hydrochloride of ethyl amidoacetate (ethyl glycocoll) is dissolved in a little water and treated with sodium nitrite; it boils at 143° C. and is decomposed by acids with evolution of nitrogen, which becomes explosively rapid if the acid be strong; it reduces hot Fehling's solution (p. 619). When it is slowly dissolved in strong ammonia it is converted into *diazoacetamide*, $N_2CH\cdot CONH_2$, which is soluble in water and forms crystals: it detonates when suddenly heated. When attacked by halogens ethyl diazoacetate exchanges its nitrogen for *two* atoms of halogen; this indicates that its constitution differs from that of diazobenzene, for instance.

By reduction, ethyl diazoacetate yields NH_3 and glycocoll, but an intermediate product is a salt of *hydraziacetic acid* which yields a hydrazine salt and glyoxylic acid when treated with an acid.

Strong NaOH saponifies and polymerises ethyl diazoacetate yielding the sodium salt of *bisdiazoacetic acid*, $CO_2H\cdot CH\langle \overset{N:N}{\underset{N:N}{\rangle}} CH\cdot CO_2H$, formerly called triazoacetic acid. The acid crystallises in orange red tables (with $2H_2O$) and gives a characteristic red colour with nitric acid. When heated with dilute acids it is hydrolysed to oxalic acid and hydrazine;

$$CO_2H\cdot CH[N_4]CH\cdot CO_2H + 2H_2SO_4 + 4H_2O = 2(N_2H_4,H_2SO_4) + 2(COOH)_2.$$

Diazomethane, $\overset{\cdot\cdot}{\underset{N}{\overset{N}{\rangle}}}CH_2$, is obtained by treating various nitroso-derivatives of methylamine such as *nitrosomethylurethane*, with alkalies:—$CO(NCH_3\cdot NO)OC_2H_5 + NaOH = CH_2N_2 + H_2O + CO(ONa)(OC_2H_5)$. When solutions of KCN and $KHSO_3$ are mixed and allowed to remain for some days, *potassium amidomethane-disulphonate*, $(SO_3K)_2:CHNH_2$, crystallises. If the mixture is warmed and then acidified the corresponding hydrogen potassium salt, $(SO_3K)(SO_3H):CHNH_2$, is obtained; this yields, when treated with KNO_2, *potassium diazomethane disulphonate*, $(SO_3K)_2C\langle \overset{\cdot\cdot}{\underset{N}{\overset{N}{\rangle}}}$, the best source of hydrazine (p. 106). Diazomethane is a yellow, odourless, poisonous gas, yielding methylhydrazine when reduced. *Diazoethane* has also been prepared.

At moderately high temperatures the aromatic amines react with nitrous acid just as the fatty amines do, the NH_2 being exchanged for OH; $C_6H_5NH_2 + ON\cdot OH = C_6H_5OH + N_2 + HOH$. But at low temperatures, particularly when a salt of the amine is employed, the diazo-compound is formed as an intermediate product—

$$\underset{\text{Aniline nitrate.}}{C_6H_5\cdot NH_2HNO_3} + ON\cdot OH = \underset{\substack{\text{Diazobenzene}\\ \text{nitrate.}}}{C_6H_5\cdot N:N\cdot NO_3} + 2HOH.$$

The salts of diazo-compounds are usually prepared in aqueous solution, since they are only used as transition-products in the preparation of other compounds (*v.i.*), or for the production of azo-compounds. The amido-compound (amine) is dissolved in a dilute acid, the solution cooled in ice, and the calculated quantity of sodium nitrite added.

For preparing the crystalline salts, amyl nitrite is the best nitrite and the reaction should be effected in absolute alcohol; the amine and the amyl nitrite

are dissolved in the alcohol, and an acid is added to the cooled solution ; after a few minutes the diazo-salt crystallises and may be washed with alcohol and ether ; $C_6H_5{\cdot}NH_2{,}HCl + C_5H_{11}NO_2 = C_6H_5{\cdot}N{:}NCl + C_5H_{11}{\cdot}OH + HOH$.

Diazobenzene nitrate is best prepared by passing N_2O_3 (p. 98) into a thin paste of aniline nitrate and water, cooled by ice and salt, until KOH no longer precipitates aniline. A brown product is filtered off, and alcohol added to the filtrate, when the nitrate separates in colourless needles. These are soluble in water, but insoluble in ether and sparingly soluble in alcohol. At 90° C., or when struck, it detonates with extreme violence.

By decomposing diazobenzene nitrate with potash, the compound $C_6H_5N_2{\cdot}OK$, *diazobenzene potassoxide*, is obtained, in which the potassium may be exchanged for other metals, producing unstable and sometimes explosive compounds. By acting on the potassium compound with acetic acid, *diazobenzene hydroxide*, $C_2H_5N_2{\cdot}OH$, is obtained as a very unstable liquid.

Diazobenzene butyrate is said to be identical in chemical behaviour and physiological effect, with *tyrotoxicon*, a poison which has been isolated from decomposing milk.

The diazo-bases, *e.g.*, $C_6H_5{\cdot}N : N{\cdot}OH$, have never been isolated owing to their instability.

The value of the diazo-compounds in effecting chemical syntheses will be appreciated from the following typical reactions when it is remembered that the conversion of an aromatic hydrocarbon into a nitro-derivative, this into an amido-derivative, and the amido- into a diazo-derivative (*diazotising*), is easily performed.

(1) For the diazo-group may be substituted a hydroxyl group by warming the compound with water, a phenol being produced ;

$$C_6H_5{\cdot}N : N{\cdot}Cl + HOH = C_6H_5{\cdot}OH + N_2 + HCl.$$

(2) The diazo-group may be exchanged for a halogen or cyanogen, producing a halogen substituted hydrocarbon or a cyanide. This is best effected by warming the diazo-compound with the corresponding cuprous salt (*Sandmeyer's reaction*). The cuprous salt forms a double compound with the diazo-salt which decomposes with the re-formation of the cuprous salt ; $C_6H_5{\cdot}N : NCl{,}Cu_2Cl_2 = C_6H_5{\cdot}Cl + N_2 + Cu_2Cl_2$.

The cuprous salt need not be pre-formed ; thus, to produce cyanobenzene (phenyl cyanide, C_6H_5CN), diazobenzene chloride may be treated with a mixture of copper sulphate and potassium cyanide (potential cuprous cyanide, p. 675). Similarly, nitro-benzene may be formed when the diazobenzene chloride is treated with KNO_2 and freshly precipitated Cu_2O (potential cuprous nitrite). Finely divided metallic copper will frequently cause the separation of nitrogen and the attachment of the acid radicle to the benzene nucleus in a diazo-salt.

The cyanides can be converted into acids by hydrolysis (p. 587), so that acids may be synthesised through Sandmeyer's reaction.

(3) For the diazo-group hydrogen may be substituted, the hydrocarbon being formed, by boiling the compound with alcohol—

$$C_6H_5{\cdot}N : NCl + C_2H_5OH = C_6H_5{\cdot}H + N_2 + HCl + CH_3{\cdot}CHO.$$

The above reactions conclusively show that diazobenzene-compounds must contain the C_6H_5 group ; that the nitrogen atoms are linked in the manner represented, is concluded from the fact that diazobenzene salts yield phenylhydrazine salts (p. 684) when reduced.

$$C_6H_5{\cdot}N : NCl + H_4 = C_6H_5{\cdot}NH{\cdot}NH_2{,}HCl.$$

On the other hand, the behaviour of solutions of the diazo-salts indicate that they are ionised by solvents in the same sense as the ammonium salts. Hence it is probable that they are really quaternary ammonium derivatives, or *diazonium*

salts of the form $\begin{matrix}C_6H_5\\Cl\end{matrix}\!\!>\!N\equiv N$, corresponding with tetramethylium chloride, $\begin{matrix}CH_3\\Cl\end{matrix}\!\!>\!N\equiv(CH_3)_3$, for example.

The salts like $C_6H_5N_2{\cdot}OK$ are apt to pass, when heated, into an unstable form which cannot be coupled readily to make an azo-compound when treated with an amine or phenol, as the normal salts can. These *isodiazo-salts* have been supposed to be really salts of the nitrosamines, of the form $C_6H_5NK{\cdot}NO$.

481. **Diazo-amido-compounds.**—When it is attempted to prepare a diazo-compound in the absence of an acid, a diazo-amido-compound is obtained; probably, one portion of the amine is diazotised and immediately combines with another portion. Thus, *diazoamidobenzene*, $C_6H_5{\cdot}N:N{\cdot}NH{\cdot}C_6H_5$, is prepared by passing N_2O_3 into a cooled solution of aniline in alcohol; diazobenzene hydroxide may be supposed to be first formed and then to combine with aniline; $C_6H_5{\cdot}N:N{\cdot}OH+NH_2{\cdot}C_6H_5=C_6H_5{\cdot}N:N{\cdot}NHC_6H_5+HOH$. It is also prepared by the interaction of diazobenzene chloride and aniline, HCl being liberated, $C_6H_5N:NCl+C_6H_5NH_2=C_6H_5N:N{\cdot}NHC_6H_5+HCl$; by substituting other primary (or secondary) amines for aniline, other diazo-amido-compounds are formed, and if two molecular proportions of diazobenzene chloride to one of the amine be used, a *disdiazo-amido*-compound is produced: $2C_6H_5N:NCl+NH_2C_6H_5=[C_6H_5N:N]_2{:}NC_6H_5+2HCl$.

Diazo-amidobenzene crystallises in yellow prisms (m.-p. 96° C.), and is not basic; like most other diazo-amido-compounds, it readily undergoes an intra-molecular transformation when in solution, becoming the corresponding *amido-azo-compound*, $C_6H_5{\cdot}N:N{\cdot}C_6H_4(NH_2)$ (*r.i.*). This is particularly liable to happen in the presence of an amine, so that during the preparation of diazo-amido-benzene the excess of aniline may cause the change. The diazo-amido-compounds are readily split up into diazobenzene compounds and aniline, so that they show most of the reactions of the former compounds.

482. **Azo-Compounds.**—When a nitro-compound is reduced in acid solution the corresponding amido-derivative is immediately produced, but when the liquid is alkaline there are formed, in the case of the aromatic nitro-compounds, three intermediate products, derived from two molecules of the nitro-compound. Thus, nitro-benzene in alkaline solution will yield *azoxybenzene*, *azobenzene* and *hydrazobenzene*, according to the reducing capacity of the agent employed.

$C_6H_5NO_2$	$C_6H_5N\!<\!\!\begin{matrix}\\O\end{matrix}\!\!>\!N{\cdot}C_6H_5$	C_6H_5N	C_6H_5NH
$C_6H_5NO_2$		C_6H_5N	C_6H_5NH
2 mols. Nitro-benzene.	Azoxybenzene.	Azobenzene.	Hydrazobenzene.

Azoxybenzene is formed when nitrobenzene is reduced by alcoholic potash, but is best prepared by oxidising azobenzene by chromic acid in acetic acid. It crystallises in yellow needles (m.-p. 36° C.), insoluble in water, but soluble in alcohol.

Azo-compounds may be *symmetrical*, like azobenzene, or *mixed*, like *benzeneazomethane*, $C_6H_5{\cdot}N:N{\cdot}CH_3$; the latter kind are produced by oxidation of the corresponding hydrazines.

Azobenzene, $C_6H_5N:NC_6H_5$, is produced when an alcoholic solution of nitrobenzene is treated with sodium amalgam or with zinc-dust and NaOH. It is readily obtained by dissolving nitrobenzene in alcohol, adding an equal weight of KOH, and distilling, when the alcohol is oxidised to acetic acid, and the nitrobenzene reduced to azobenzene. At the end of the distillation it comes over as a dark red oil, which solidifies after a time to a crystalline mass; it is insoluble in water, but may be

crystallised from alcohol or ether in beautiful red tables resembling $K_2Cr_2O_7$; it melts at 68° C. and boils at 293° C.

Azobenzene is also formed when aniline is oxidised with $KMnO_4$. It forms substitution products like benzene does. Alkaline reducing-agents convert it into hydrazobenzene, but acid reducing-agents convert it into aniline.

483. **Azo-dyestuffs.**—Since the dyeing of a fabric involves the formation of an insoluble coloured substance in the fibre, it is essential that a *dyestuff* shall be capable of combining either with the fibre itself or with some substance (a *mordant*) previously fixed in the fibre, to form an insoluble compound (the *dye*). Most dyestuffs are capable of forming dyes with wool, and to a smaller extent with silk, without the intervention of a mordant; the dyes thus produced are termed *substantive dyes*. With cotton, on the other hand, a mordant is nearly always requisite, the dye obtained being called, in this case, an *adjective dye*. It will be seen that since a dyestuff must enter into some form of chemical combination before it can become a dye, it must be a substance possessed of a certain amount of chemical activity. Thus it happens that those substances which have been found to be successful dyestuffs are generally either acid or basic in character; this observation has proved of great value, since it has shown that although a compound may be useless as a dyestuff it may become useful if it be treated in such a manner that the necessary acidity or basicity be imparted to it. It is possible to impart acidity to an organic compound by the introduction of certain radicles, such as OH or SO_2OH, and basicity by introducing the NH_2 radicle. It is, of course, only certain organic compounds* which can be converted into dyestuffs by the introduction of such groups; these compounds are called *chromogens*, whilst the groups that lend them their dyeing capacity are called *auxochromes*. An acid auxochrome yields an *acid dyestuff*, capable of being fixed by a basic mordant (alumina, &c.); whilst a basic auxochrome yields a *basic* dyestuff, capable of being fixed by an acid mordant (tannin). That a dyestuff must be soluble in water hardly needs stating; it will be equally obvious that a dyestuff need not be itself a coloured substance, although the insoluble compound which it forms in the fibre must be coloured.

Azobenzene is a highly coloured substance, but is at the same time both chemically indifferent and insoluble in water, so that it is not a dyestuff. It is, however, a chromogen, for, by the introduction of the OH or NH_2 group, compounds are produced which are either dyestuffs (when soluble in water) or become dyestuffs when rendered soluble by conversion into sulphonic acids.

The *diazo-dyestuffs* are compounds containing the ·N : N· group and are made by diazotising an amido-compound and combining the product with an amido- or hydroxy-compound (a "dyestuff component").

Amido-azo-compounds are produced by the intramolecular change of diazo-amido-compounds (p. 682), especially in presence of the salt of an amine which, however, is not consumed. The change generally produces an amido-azo-compound in which the amido-group is in the para-position to the azo-group, hence if an aromatic amine is used to prepare the diazo-amido-compound, the para-position to the amido-group should be unoccupied.

p-Amido-azobenzene is prepared by heating diazo-amidobenzene (10 grams) with aniline hydrochloride (5 grams) and aniline (25 grams) at 45° C., dissolving out the amiline with acetic acid and crystallising the residue from HCl. The hydrochloride thus formed is in steel-blue needles and was formerly sold as *aniline yellow*, a dyestuff. The base, liberated by NH_3 from the hydrochloride, forms yellow needles and melts at 127° C. By sulphonation it yields a mixture of mono- and di-sulphonic acids, known as *acid yellow* or *fast yellow*. It is largely used for making indulines (*q.v.*). By reduction, amido-azobenzene yields aniline and paraphenylenediamine.

Dimethylamidobenzenesulphonic acid is prepared from diazo-benzenesulphonic acid chloride and dimethylaniline—

$C_6H_4(SO_3H)\cdot N : N\cdot Cl + C_6H_5\cdot N(CH_3)_2 = C_6H_4(SO_3H)\cdot N : N\cdot C_6H_4N(CH_3)_2 + HCl$.

The sodium salt is *methyl orange* (*tropæolin O*, *helianthin* or *orange III.*), used in the laboratory as an indicator.

2 : 4-*Diamidoazobenzene*, $C_6H_5\cdot N : N\cdot C_6H_3(NH_2)_2$, is made by the action of diazobenzene chloride on metaphenylene-diamine—$C_6H_5N : NCl + C_6H_4(NH_2)_2 = C_6H_5\cdot N : N\cdot C_6H_3(NH_2)_2 + HCl$. It melts at 117° C. and its hydrochloride is an orange

* Almost always such as contain one or more benzene nuclei, and a special group, like the diazo-group, called a *chromophore*.

yellow dyestuff called *chrysoidine*. The 4 : 4'-*diamido-azobenzene*, $NH_2 \cdot C_6H_4 \cdot N : N \cdot C_6H_4 \cdot NH_2$ gives rise to the red basic dyestuffs, the *azylines*, which are the tetra-alkyl derivatives of the above compound and are obtained by diazotising a dialkyl-*p*-phenylenediamine and combining the product with a dialkylaniline—

$$NR_2 \cdot C_6H_4 \cdot N : N \cdot Cl + C_6H_5NR_2 = NR_2 \cdot C_6H_4 \cdot N : N \cdot C_6H_4 \cdot NR_2 + HCl.$$

Bismarck brown (*phenylene brown*, Manchester brown) is the hydrochloride of a mixture of bases prepared by the action of nitrous acid on metaphenylendiamine; it consists largely of the hydrochloride of *triamido-azobenzene*, $C_6H_4(NH_2) \cdot N : N \cdot C_6H_3(NH_2)_2$, formed by diazotising one NH_2 in the metaphenylene-diamine and combining the diazo-compound with another mol. of the diamine.

Hydroxyazo-compounds are prepared by the interaction of a diazo-chloride and a phenol. Thus *hydroxyazo-benzene* is prepared from diazo-benzene chloride, and phenol; $C_6H_5 \cdot N : N \cdot Cl + C_6H_5OH = C_6H_5 \cdot N : N \cdot C_6H_4(OH) + HCl$. They are also formed by an intra-molecular change of the azoxy-compounds, just as the amidoazo-result from the diazoamido-compounds.

Dihydroxyazobenzenesulphonic acid, $C_6H_4(SO_3H) \cdot N : N \cdot C_6H_3(OH)_2$, is prepared from the chloride of diazobenzenesulphonic acid and resorcinol (*cf. methyl orange*). Its sodium salt is *resorcin yellow*.

Diazo-dyestuffs.—These contain the $\cdot N : N \cdot$ group twice, and are of three kinds. (1) The two N_2 groups may be attached to the same benzene nucleus which also contains the auxochrome (OH or NH_2). For instance, by the reaction of diazo-benzene chloride on resorcinolazobenzene, *resorcinoldiazobenzene* is obtained—$C_6H_5N_2Cl + C_6H_5N_2C_6H_3(OH)_2 = C_6H_5 \cdot N : N \cdot C_6H_2(OH)_2 \cdot N : N \cdot C_6H_5 + HCl$. (2) The two N_2 groups may be attached to the same benzene nucleus and the auxochrome to another nucleus. *Biebrich scarlet* is a dyestuff of this type made by diazotising amidoazobenzene disulphonic acid to produce

$$C_6H_4(SO_3H) \cdot N : N \cdot C_6H_3(SO_3H) \cdot N : N \cdot Cl,$$

which is then combined with β-naphthol, producing

$$C_6H_4(SO_3H) \cdot N : N \cdot C_6H_3(SO_3H) \cdot N : N \cdot C_{10}H_6(OH).$$

(3) The two N_2 groups may be attached to different nuclei. To this class belong the numerous *benzidine dyestuffs* or *tetrazo-dyestuffs*, which are valuable as substantive dyestuffs for cotton, most others requiring a mordant. *Congo-red* serves as a type; benzidine, $NH_2 \cdot C_6H_4 - C_6H_4 \cdot NH_2$ (p. 666) is diazotised to *tetrazodiphenyl chloride*, $ClN : N \cdot C_6H_4 - C_6H_4 \cdot N : NCl$, which is then combined with *α-naphthylaminesulphonic acid*, $C_{10}H_6(SO_3H) \cdot NH_2$ to form congo-red, the formula for which is $NH_2 \cdot (SO_3Na)C_{10}H_5 \cdot N : N \cdot C_6H_4 - C_6H_4 \cdot N : N \cdot C_{10}H_5(SO_3Na) \cdot NH_2$.

Derivatives of Hydrazine and Hydrogen Nitride (Diazoimides).

484. **Hydrazines.**—These bases are derived from hydrazine (p. 106), $H_2N \cdot NH_2$, by substituting a hydrocarbon radicle for H. They may be *primary*, $R \cdot NH \cdot NH_2$, or *secondary*, $R_2 : N \cdot NH_2$, and *symmetrical*. $RHN \cdot NHR$ (*hydrazo-compounds*), or *asymmetrical*, $RHN \cdot NH_2$ (*hydrazine compounds*). When R is an alkyl radicle, the hydrazines are best prepared by the action of reducing-agents on the nitrosoamines; $R_2 : N \cdot NO + H_4 = R_2 : N \cdot NH_2 + H_2O$. But the alkyl hydrazines are of very little importance at present. When R is an aromatic radicle, the hydrazines are best prepared by the reduction of the diazo-compounds. The reaction of the hydrazines with compounds containing ketonic or aldehydic oxygen has been already noticed (pp. 583, 625).

Phenylhydrazine, $C_6H_5 \cdot NH \cdot NH_2$, is prepared by dissolving aniline (1 part by weight) in strong HCl (20 parts), cooling by adding ice, and slowly adding an ice-cold solution of $NaNO_2$ (0.75 parts), in water (4 parts). The aniline hydrochloride is thus converted into di-azobenzene chloride (p. 680). A solution of stannous chloride (4.5 parts) in an equal weight of HCl is now carefully added; this converts the

diazobenzene chloride into phenylhydrazine hydrochloride, which is precipitated—

$$C_6H_5N : N{\cdot}Cl + 4HCl + 2SnCl_2 = C_6H_5{\cdot}NH{\cdot}NH_2{,}HCl + 2SnCl_4.$$

The precipitate is washed with a mixture of alcohol and ether, dissolved in a little water, and decomposed by strong NaOH, when the hydrazine separates as an oily layer, which is freed from water by distilling with potassium carbonate.

Phenylhydrazine is thus obtained as a colourless aromatic liquid of sp. gr. 1.091, and boiling-point 241° C. It solidifies in a freezing mixture to tabular crystals, fusing at 23° C. It is sparingly soluble in cold water, but dissolves in alcohol and ether. Phenylhydrazine is a strong reducing-agent and absorbs oxygen from air, becoming brown. It reduces alkaline cupric solution, *even in the cold*, precipitating yellow cuprous hydroxide, and evolving nitrogen, while aniline and benzene are found in the solution. This is a *general reaction for identifying hydrazines*, and may also be employed for diazo-compounds by boiling their aqueous solutions with $KHSO_3$, to reduce them to hydrazines, and adding potash and alkaline cupric solution. It also reduces mercuric oxide in the cold, forming nitrogen, aniline, benzene, and mercury-diphenyl. It is a monacid base, and forms crystalline salts. Solution of phenylhydrazine hydrochloride, mixed with sodium acetate, forms a *general test for aldehydes and ketones*, with which it forms insoluble oily or crystalline compounds (*hydrazones*, p. 625, see also *osazones*), thus precipitating them from their aqueous solutions; by warming these compounds with HCl they are reconverted into their parent substances. When heated with nascent hydrogen phenylhydrazine yields $C_6H_5NH_2$ and NH_3, a fact which settles its constitution, as well as that of the other hydrazines. It is used technically for making antipyrine (*q.v.*)

Sodium dissolves in phenylhydrazine evolving H and forming $C_6H_5NaN{\cdot}NH_2$.

Hydrazine yields derivatives on the same lines as NH_3 does, but as it has four H atoms and two N atoms, the latter allowing of dissymmetry, the number of such derivatives is even greater than that obtainable from NH_3. Moreover, the hydrazine derivatives have a remarkable tendency to undergo internal condensation, yielding nitrogen ring compounds (*cf.* antipyrine). The following are the leading types:

(1) *Asymmetrical* and *secondary hydrazines*; *hydrazonium* and *azonium* compounds, corresponding with the amines. *Hydrazobenzene* or *sym-diphenyl-hydrazine*, $C_6H_5HN{\cdot}NHC_6H_5$ (p. 684), is prepared by dissolving azobenzene in alcohol, passing NH_3, and afterwards H_2S till the solution is colourless.

$$C_6H_5N : NC_6H_5 + H_2S = C_6H_5HN{\cdot}NHC_6H_5 + S.$$

On adding water, the hydrazobenzene is precipitated, and may be crystallised from alcohol. It forms colourless tables (m.-p. 131° C.) becoming orange in air, from production of azobenzene, and smelling of camphor. A convenient method of converting azobenzene into hydrazobenzene is to boil its alcoholic solution with zinc-dust until it is colourless.

When heated, hydrazobenzene is decomposed into azobenzene and aniline—

$$2(C_6H_5HN{\cdot}NHC_6H_5) = C_6H_5N{\cdot}NC_6H_5 + 2(C_6H_5{\cdot}H_2N).$$

When dissolved in hydrochloric or sulphuric acid, it is converted into its metameride benzidine, $NH_2C_6H_4{\cdot}C_6H_4NH_2$ (p. 666). This change recalls that of a diazoamido-compound into an amido-azo-compound (p. 682) and like the latter only occurs when the 4-positions in the benzene rings are free. Thus *o-* or *m-hydrazotoluene* yields *tolidine* by this intramolecular change (*benzidine migration*), but in *p*-hydrazotoluene only one of the NH groups shifts (*semidine migration*), producing $C_7H_7NHC_7H_6NH_2$, in which NH_2 is in the 2-position. These changes may also be compared with that of methylaniline into paratoluidine (p. 665), and it

should be noted that all migrations of this type tend to produce a compound of more basic properties.

Examples of other hydrazines of this class are *α-* and *β-ethylphenylhydrazine*, $C_6H_5N(C_2H_5)\cdot NH_2$ and $C_6H_5HN\cdot NHC_2H_5$. The former combines with C_2H_5Br forming *diethylphenylhydrazonium bromide*, $C_6H_5N(C_2H_5)_2Br\cdot NH_2$, while *αβ-diethylphenylhydrazine*, $C_6H_5N(C_2H_5)\cdot NHC_2H_5$, combines with C_2H_5Br to form the *azonium* compound, $C_6H_5N(C_2H_5)_2Br\cdot NHC_2H_5$.

(2) *Phenylhydrazones.*—Already noticed (p. 685).

(3) *Hydrazides.*—These are acidyl derivatives corresponding with the amides and prepared analogously. For example, *α-acetylphenylhydrazide*, $C_6H_5N(CH_3CO)\cdot NH_2$, from sodium phenylhydrazine and acetyl chloride (m.-p. 124° C.).

Semicarbazide, $NH_2CO\cdot NH\cdot NH_2$, may be regarded as the hydrazide of carbamic acid, and is obtained by heating urea with hydrazine sulphate at 100° C. It gives rise to many derivatives, combining with aldehydes and ketones as phenylhydrazine does; the products are called *semicarbazones*.

(4) *Hydrazido-acids* are like amido-acids and are either symmetrical, *e.g.*, $C_6H_5NH\cdot NH\cdot CH_2COOH$, or asymmetrical, *e.g.*, $C_6H_5N(NH_2)\cdot CH_2COOH$.

(5) *Hydrazidines* (*amidoazones*) are analogues of the amidines (p. 668), the NH group of the latter having been exchanged for the phenylhydrazone group, producing compounds of the type, $RC\langle^{N\cdot NHC_6H_5}_{NH_2}$. When the NH_2 group is exchanged for the diazobenzene group, *formazyl-derivatives* are obtained, $RC\langle^{N\cdot NHC_6H_5}_{N:NC_6H_5}$, which are highly coloured and may be viewed as azo-dyestuffs, prepared from diazobenzene and phenylhydrazones.

(6) *Tetrazones* are produced when two mols. of a secondary hydrazine are oxidised with HgO—

$$2C_6H_5N(CH_3)\cdot NH_2 + O_2 = C_6H_5N(CH_3)\cdot N:N\cdot(CH_3)NC_6H_5.$$

485. **Diazoimides.**—The derivatives of hydrogen nitride, or azoimide, HN_3 (p. 107), are also called *diazoimides*, or *triazo-compounds*. They are obtainable by the action of NH_3 on the *diazo-perbromides*. Thus, when diazobenzene bromide is brominated, $C_6H_5\cdot N:NBr + Br_2 = C_6H_5\cdot NBr\cdot NBr_2$; when the perbromide is treated with ammonia, $C_6H_5\cdot NBr\cdot NBr_2 + NH_3 = 3HBr + C_6H_5\cdot N\langle^{N}_{N}$ (*phenylazoimide*). When heated with alcoholic potash the *dinitro-phenylazoimide* yields dinitrophenol and potassium nitride, KN_3.

Benzoyl azoimide, $C_6H_5CO\cdot N_3$, formed when *benzoyl-hydrazide*, $C_6H_5CO\cdot NH\cdot NH_2$, is diazotised, yields sodium benzoate and sodium nitride when boiled with NaOH.

X. CYANOGEN AND ITS COMPOUNDS.

486. In the beginning of the eighteenth century, a manufacturer of colours at Berlin accidentally obtained a blue powder when precipitating sulphate of iron with potash. This substance was used as a colour under the name of *Prussian blue*, for several years, before any explanation of its production was attempted, or even before the conditions under which it was formed were exactly determined. It 1724 it was shown that Prussian blue could be prepared by calcining dried animal matters with potashes, and mixing the aqueous solution of the calcined mass, first with sulphate of iron and afterwards with hydrochloric acid; but the most important step towards the determination of its composition was made by Maquer, who found that, by boiling it with an alkali, Prussian blue was decomposed, yielding a residue of red oxide of iron, and a solution which reproduced the blue when mixed with a salt of iron; hence he inferred that the colour was a compound of the oxide of iron with an acid for which the alkali had a more powerful attraction—

a belief, confirmed in 1782, by Scheele's observations, that when an alkaline solution prepared for making the blue was exposed to the air, or to the action of carbonic acid, it lost the power of furnishing the colour, but the escaping vapour struck a blue on paper impregnated with oxide of iron. Scheele also prepared this acid in a pure state, and it soon after obtained the name of *prussic acid*.

In 1787, Berthollet found prussic acid to be composed of carbon, hydrogen, and nitrogen, but he also showed that the power of the alkaline liquor to produce Prussian blue depended upon the presence of a yellow salt crystallising in octahedra, and containing prussic acid, potash, and oxide of iron, though the latter was so intimately bound up with the other constituents that it could not be separated by those substances which are usually employed to precipitate iron.

Porrett, in 1814, applying the greatly increased resources of chemistry to the investigation of this subject, decomposed Prussian blue with baryta, and subsequently removed the baryta from the salt thus obtained by means of sulphuric acid, when he obtained a solution of the acid, which he named *ferruretted chyazic acid*.

In 1815, Gay-Lussac, having boiled Prussian blue (or prussiate of iron, as it was then called) with red oxide of mercury and water, and crystallised the so-called prussiate of mercury, exposed it, in the dry state, to the action of heat, and obtained a gas having the composition CN, which was called *cyanogen*,* in allusion to its connection with Prussian blue. It was then seen that the substance which had been called ferruretted chyazic acid contained iron and the elements of cyanogen, whence it was called *ferrocyanic acid*, and its salts were spoken of as ferrocyanates. Robiquet first obtained this acid in the crystallised state, having the composition $C_6H_4N_6Fe$; and since it was found that, when brought in contact with metallic oxides, it exchanged the H, for an equivalent quantity of the metal, according to the equation, $H_4 \cdot C_6N_6Fe + 2M''O = M_2'' \cdot C_6N_6Fe + 2H_2O$, it was concluded that the C_6N_6Fe composed a distinct group or radicle, which was named *ferrocyanogen* (Fcy), the acid being called *hydroferrocyanic acid*, and the salts *ferrocyanides*.

487. **Cyanogen and Cyanides.**—*Cyanogen*, $(CN)_2$ or NC·CN, is obtained by heating mercuric cyanide in a glass tube or retort (Fig. 282), and collecting the gas over mercury; $Hg(CN)_2 = Hg + (CN)_2$; the metallic mercury collects in globules on the cool glass. The whole of the cyanogen is not obtained, part being converted into a brown solid called *paracyanogen*, which is left behind. This is polymeric with cyanogen, into which it may be converted by a high temperature. By heating together solutions of potassium cyanide and $CuSO_4$, cyanogen is evolved; $2CuSO_4 + 4KCN = Cu_2(CN)_2 + (CN)_2 + 2K_2SO_4$.

Fig. 282.

Cyanogen is identified by its remarkable odour, and by its burning with a pink flame edged with green. Its sp. gr. is 1.806 (air = 1), and it may therefore be collected by displacement of air. It is easily liquefied by a pressure of 4 atmospheres at 15° C. and 1½ atmosphere

* From κυάνεος, blue.

at 0° C. Liquid cyanogen has sp. gr. 0.87, and solidifies to a crystalline mass at $-34°$ C. and boils at $-21°$ C. Water dissolves about 4 volumes of cyanogen, yielding a solution which soon deposits a brown flocculent substance termed *azulmic acid*, $C_4N_5H_3O$. The solution is then found to contain ammonium salts, especially carbonate, formate, and oxalate, together with urea.

The first reaction between cyanogen and water, on standing, probably resembles that between chlorine and KOH in the cold, viz., $Cl_2 + 2KOH = KCl + KClO + H_2O$; the reaction in the case of cyanogen being $(CN)_2 + H_2O = HCN + H(CN)O$, producing hydrocyanic, HCN, and cyanic, HCNO, acids. The cyanic acid yields NH_4HCO_3 by reaction with water; $HCNO + 2H_2O = NH_4HCO_3$. Hydrocyanic acid, with water, yields ammonium formate; $HCN + 2H_2O = HCO_2NH_4$. Cyanogen, with water, yields ammonium oxalate; $(CN)_2 + 4H_2O = C_2O_4(NH_4)_2$. Cyanic acid, with ammonia, yields urea; $HCNO + NH_3 = (NH_2)_2CO$. The azulmic acid appears to result from a reaction between cyanogen, ammonia, and water; $2(CN)_2 + NH_3 + H_2O = C_4H_5N_5O$; it may be prepared by passing cyanogen into dilute ammonia, and heating in a closed vessel. When dry ammonia gas acts upon cyanogen gas, a black substance is produced, which is called *hydrazulmin*: $2NH_3 + 2(CN)_2 = C_4H_6N_6$. This appears to be *azulmamide*, for, when acted on by water, it yields azulmic acid and ammonia; $C_4H_6N_6 + H_2O = C_4H_5N_5O + NH_3$.

In most of its reactions, cyanogen exhibits the mutability which is generally observed in organic groups, but in some cases it exhibits a stability which allows it to be compared with the halogens. Thus, alkali metals take fire in cyanogen when gently heated, producing their respective cyanides; $K_2 + (CN)_2 = 2KCN$; cyanogen, acting on solution of potash, yields potassium cyanide and cyanate; $(CN)_2 + 2KOH = KCN + KCNO + H_2O$, just as chlorine yields chloride and hypochlorite. Cyanogen combines with H, under influence of the silent electric discharge, to form hydrocyanic acid, H(CN), which forms cyanides by exchanging its hydrogen for metals, just as hydrochloric acid forms chlorides; but the cyanides of potassium and sodium are much less stable compounds than the corresponding chlorides. When boiled with water, the alkali cyanides are converted into alkali formates, the nitrogen being evolved as NH_3, and the carbon converted into the COOH group; $KCN''' + 2H_2O = KCO''(OH)' + NH_3$.

The facility with which *the CN group is transformed by hydrolysis into the CO_2H group*, is of very great importance in organic research, since it is often easy to introduce the CN group into an organic molecule, and, by afterwards converting it into CO_2H, to effect the synthetical formation of an organic acid, as has been already explained (p. 587).

Cyanogen is produced in small quantity by the direct union of carbon and nitrogen at the extremely high temperature of the electric spark, but to produce it in quantity, one, at least, of its elements must be in the form of a compound; thus, if ammonia be passed over red-hot charcoal, hydrogen cyanide is produced; $NH_3 + C = HCN + H_2$; again, if acetylene is mixed with nitrogen and "sparked," hydrogen cyanide is formed, $C_2H_2 + N_2 = 2HCN$. If one of the alkali metals be present, nitrogen is much more easily converted into cyanogen; potassium cyanide may be obtained by passing nitrogen through an iron tube containing a heated mixture of charcoal and potassium—$N_2 + C_2 + K_2 = 2KCN$. In place of the costly potassium, the materials for making it, viz., potassium carbonate and charcoal, may be used (see below). A better yield is obtained by employing a compound of nitrogen with

carbon, such as refuse horn or cuttings of hides and old leather, which are rich in nitrogen.

On a large scale, potassium cyanide is made in this way, but as it cannot be crystallised easily, it is converted into the ferrocyanide, which is the source whence all cyanogen compounds are obtained.

488. **Potassium ferrocyanide**, $K_4FeC_6N_6.3Aq$ or $4KCN.Fe''(CN)_2.3Aq$, *yellow prussiate of potash*, is manufactured by melting potashes (crude K_2CO_3) mixed with iron filings in an iron vessel, and adding any cheap material containing carbon and nitrogen, such as old leather. Sometimes the animal matter is distilled for the sake of the ammonia which it will yield, and the remaining charcoal, still rich in nitrogen, is used for making ferrocyanide. The fused mass is heated with water in open boilers, when a yellow solution is obtained, which, after evaporation, deposits truncated pyramidal crystals of potassium ferrocyanide.

The chemistry of this process is somewhat abstruse, but is generally explained as follows: (1) The carbon containing nitrogen decomposes the potassium carbonate at a high temperature, producing potassium cyanide and CO; $K_2CO_3 + C_4 + N_2 = 2KCN + 3CO$. (2) Sulphur, derived from the animal matters, and partly from potassium sulphate present as an impurity in the potashes, combines with iron to form ferrous sulphide. (3) On treating the fused mass with water, the ferrous sulphide is dissolved by the KCN, yielding potassium sulphide and ferrocyanide; $FeS + 6KCN = K_4Fe(CN)_6 + K_2S$.

It has been suggested to avoid the presence of K_2S in the liquor (which hinders crystallisation) by melting pure K_2CO_3 with animal charcoal, extracting the KCN from the residue by treatment with water, and digesting with finely ground spathic iron ore ($FeCO_3$); $FeCO_3 + 6KCN = K_4Fe(CN)_6 + K_2CO_3$.

The ferrocyanide dissolves in twice its weight of boiling and in four times its weight of cold water, but is insoluble in alcohol. The aqueous solution assumes a darker yellow colour when exposed to air for some time, oxygen being absorbed and potassium ferricyanide (see below) produced in small quantity. The neutral solution then becomes slightly alkaline from formation of potash.

Crystallised ferrocyanide does not lose water till 60° C., when it gradually becomes white and opaque. At 100° C. it may be dried completely, though with difficulty, unless finely powdered and heated in a current of dried air. When the undried salt is moderately heated, it evolves ammonia and hydrocyanic acid, and becomes brown. The thoroughly dried salt does not evolve ammonia, but fuses at a high temperature, evolving nitrogen, and leaving a residue of potassium cyanide and iron carbide; $K_4C_6N_6Fe = N_2 + 4KCN + FeC_2$.

Nearly all acids decompose the ferrocyanide, evolving hydrocyanic acid, and producing compounds containing cyanogen and iron, which become blue when exposed to air, from the formation of Prussian blue and similar compounds. It is for this reason that the yellow crystals become blue and green when exposed to the air of a laboratory. Oxidising-agents convert the ferrocyanide into ferricyanide, as will be seen later. With a large number of metallic salts, the ferrocyanide gives precipitates, so that it is an indispensable test. It is also largely employed in the manufacture of colours, and in dyeing and calico-printing. The constitution and chemical relations of the ferrocyanides will be better understood later in the history of cyanogen compounds.

Hydrogen cyanide, hydrocyanic, or prussic acid, H.C ⋮ N (or HCy), is prepared, in aqueous solution, by distilling potassium ferrocyanide (*prussiate of potash*) with dilute H_2SO_4. 50 grammes of the crystallised ferrocyanide are dissolved in 200 cubic centimetres of warm water in a flask or retort connected with a good condenser. 20 c.c. of strong sulphuric acid are diluted with 60 c.c. of water, cooled, and added to the solution of ferrocyanide; heat is applied by a ring-burner to avoid bumping, until about 140 c.c. of liquid has passed into the receiver.

The potassium ferrocyanide gives up half of the cyanogen, CN, as hydrocyanic acid, leaving the remainder combined with the iron and half of the potassium as *potassio-ferrous ferrocyanide*, $K_2Fe''.Fe''(CN)_6$, a yellow salt which quickly becomes blue when exposed to air, oxygen being absorbed, and *Prussian blue*, or *ferric ferrocyanide*, $Fe'''_4.3Fe''(CN)_6$, produced. The following equation represents the preparation of hydrocyanic acid; $2K_4FeCy_6 + 6H_2SO_4 = 6HCy + K_2Fe''_2Cy_6 + 6KHSO_4$.

Hydrocyanic acid is generally used diluted, but it may be obtained anhydrous by gently heating the diluted acid in a retort connected with a condenser cooled by iced water, and receiving the distillate in a bottle cooled in ice and containing fused calcium chloride in coarse powder. This bottle is afterwards placed in a water-bath connected with a receiver cooled in ice and salt, and gently heated, when the pure hydrocyanic acid distils over. The anhydrous HCy may also be obtained by passing dry H_2S gas into a long tube filled with mercuric cyanide and connected with a receiver cooled in ice and salt: the operation must be stopped when an inch or two of mercuric cyanide remains undecomposed, to avoid contamination of the HCy with H_2S; $HgCy_2 + H_2S = HgS + 2HCy$.

Properties of hydrocyanic acid.—A colourless liquid, sp. gr. 0.7, which evaporates rapidly, so that a few drops in a watch-glass are solidified by the cold of evaporation, the freezing-point being − 12° C. The acid boils at 25° C., and its vapour burns with a purple flame. The smell of the vapour is quite characteristic, and is compared by some to a faint odour of almonds; it generally produces a sensation of dryness at the back of the throat. The inhalation of the vapour, unless largely diluted with air, is very dangerous, and an extremely small quantity of the acid taken internally generally kills immediately. When the pure acid is mixed with an equal volume of water, a contraction ensues, amounting to about one-twentieth of the total volume, and *cold* is produced. The aqueous acid is decomposed when exposed to light, depositing a brown substance, whilst ammonia formate and other products are found in solution; $HCN + 2H_2O = H{\cdot}CO_2NH_4$. A trace of sulphuric acid, which generally splashes over in preparing prussic acid, prevents this decomposition. Acids and alkalis, when boiled with the acid, convert the HCN into formic acid and ammonia.

The acid properties of HCy are very feeble; it hardly reddens litmus, and does not destroy the alkaline reaction of the alkalies or their carbonates. The salts formed by displacing its hydrogen by alkali-metals are easily decomposed by water and carbonic acid, and therefore smell of HCy, but the cyanides formed by many of the metals are very stable bodies.

Although HCy is so much more easily liquefied than HCl, its vapour continually escapes even from a weak aqueous solution, so that the strength is diminished every time the stopper is removed from the bottle; it thus happens that the weak prussic acid (2 per cent.) dis-

pensed by the druggists, is sometimes found to have become nearly pure water.

Hydrocyanic acid is found in laurel-water, and in water distilled from the kernels of many stone-fruits, such as peach, apricot, and plum. In these cases it appears to be produced from amygdalin (see p. 584).

Hydrocyanic acid is produced synthetically by passing a succession of electric sparks through a mixture of nitrogen with an equal volume of acetylene, this being itself produced by carbon intensely heated in hydrogen (p. 100). HCy is also found among the products of distillation of coal, and occurs in imperfectly-purified coal-gas.

Tests for hydrocyanic acid.—Silver nitrate produces a white precipitate of silver cyanide, AgCN, which is dissolved by boiling with strong nitric acid, and precipitated in microscopic needles, $AgCN.2AgNO_3$, on cooling. *Prussian-blue test:* Add potash in slight excess, to form KCy; then add ferrous sulphate solution (which always contains ferric sulphate),* to form potassium ferrocyanide: $6KCy + Fe''SO_4 = K_4Fe''Cy_6 + K_2SO_4$; this acts on the ferric sulphate, and produces ferric ferrocyanide, or Prussian blue: $3K_4Fe''Cy_6 + 2Fe'''_2(SO_4)_3 = Fe'''_4(Fe''Cy_6)_3 + 6K_2SO_4$. But the excess of potash decomposes the blue; to correct this, add excess of hydrochloric acid to neutralise the potash, the blue will then be visible. *Sulphocyanide test:* Add yellow ammonium sulphide (which contains some disulphide), to form ammonium sulphocyanide; $HCN + (NH_4)_2S_2 = NH_4CNS + NH_4HS$; evaporate till the smell of ammonium hydrosulphide has disappeared, and add ferric chloride, which will produce the blood-red colour of ferric sulphocyanide, bleached on adding mercuric chloride. A very fugitive purple colour is due to ammonium thiosulphate produced by the action of air, and does not indicate HCy.

Potassium cyanide, KCN, or KCy, is prepared by fusing, in an iron crucible, a mixture of well-dried potassium ferrocyanide (8 parts) with dried K_2CO_3 (3 parts); $K_4Cy_6Fe + K_2CO_3 = 5KCy + KCyO + Fe + CO_2$. As soon as the escape of CO_2 has ceased, and the metallic iron has subsided, the clear fused mixture of cyanide and cyanate of potassium is poured into an iron mould. The presence of cyanate does not interfere with most of the uses of the cyanide; its quantity may be diminished by adding some powdered charcoal to the mixture.

A purer product is obtained, though less economically, by fusing the dried ferrocyanide alone (see above), and crystallising the product by dissolving in hot alcohol. The purest potassium cyanide is made by passing vapour of hydrocyanic acid into solution of potash in absolute alcohol, when the cyanide is deposited in small octahedral crystals.

Potassium cyanide, as met with in commerce, is in white opaque lumps, and contains about 98 per cent. of cyanide, the rest being cyanate and carbonate. When exposed to air, it deliquesces, and smells of hydrocyanic acid and ammonia, the former being produced from the cyanide, and the latter from the cyanate, by the action of water—

(1) $KCN + H_2O = KOH + HCN$. (2) $KCNO + 2H_2O = NH_3 + KHCO_3$.

It dissolves very readily in water, yielding a strongly alkaline solution, which evolves HCy and NH_3 when boiled, and becomes a solution of potassium formate; $KCN + 2H_2O = NH_3 + HCO_2K$. When the commercial cyanide is boiled with moderately strong alcohol, the cyanide, together with a little cyanate, is dissolved, and may be crystallised from the solution, while the carbonate is left undissolved. Potassium cyanide fuses at a low red heat, becoming very fluid; it then

* It is well either to shake with air or to add a drop of ferric chloride to ensure the presence of ferric salt.

absorbs oxygen from the air, forming cyanate. This disposition to combine with oxygen causes it to act as a powerful reducing-agent upon metallic oxides; tin-stone is assayed by fusing it with potassium cyanide, when a button of tin collects at the bottom of the fused mass; $SnO_2 + 2KCy = Sn + 2KCyO$. When heated with KNO_3 or $KClO_3$, it causes a violent explosion, from evolution of CO_2 and N.

Pure potassium cyanide is alkaline, but does not effervesce with acids, like the commercial cyanide. Solution of potassium cyanide dissolves silver chloride and iodide, which leads to its use in electro-plating and in photography, while its property of dissolving silver sulphide is useful in cleaning gold and silver. It is one of the most dangerous poisons. It is also used in gold-extraction (p. 514), for which purpose it may be made by heating K_4FeCy_6 with sodium; $K_4FeCy_6 + Na_2 = 4KCy + 2NaCy + Fe$. The product is a mixture of the two cyanides which is as effective as pure KCN.

Potassium cyanide is sometimes obtained in considerable quantity from the blast-furnaces of iron-works being formed from the potassium carbonate in the ash of the fuel.

Ammonium cyanide, NH_4CN, may be sublimed in cubes by heating a mixture of mercuric cyanide and ammonium chloride. It dissociates, at 36° C., into NH_3 and HCN. It is very soluble in water and alcohol, and smells of hydrocyanic acid and ammonia. When kept it becomes brown, azulmin being produced (p. 688).

The *cyanides* of *barium*, *strontium*, and *calcium* are less soluble than the alkali cyanides, and are easily decomposed by carbonic acid. *Zinc cyanide*, $ZnCy_2$, is precipitated by KCy from $ZnSO_4$; it dissolves in KCy, forming $ZnCy_2(KCy)_2$ which crystallises in octahedra. *Nickel cyanide*, $NiCy_2$, obtained in a similar way, forms a pale green precipitate, readily soluble in excess, forming $NiCy_2(KCy)_2$, from which hydrochloric acid re-precipitates the nickel cyanide—

$$NiCy_2(KCy)_2 + 2HCl = NiCy_2 + 2KCl + 2HCy.$$

If the solution of nickel cyanide in potassium cyanide be heated with mercuric oxide, nickel oxide is precipitated: $NiCy_2(KCy)_2 + HgO = HgCy_2(KCy)_2 + NiO$. This reaction is important in quantitative analysis. Nickel cyanide is remarkable for its insolubility even in boiling hydrochloric acid.

489. *Cobalt cyanide*, $CoCy_2$, is precipitated of a reddish-brown colour when potassium cyanide is added to cobalt nitrate; it dissolves easily in excess of potassium cyanide, forming *potassium cobaltocyanide*, $K_4(CoCy_6)$, which may be obtained in red deliquescent crystals by adding alcohol. This compound corresponds with potassium ferrocyanide, $K_4(FeCy_6)$, but is far less stable: when exposed to air, or boiled with water, it undergoes oxidation, the cobaltous compound being converted into a cobaltic compound, the *potassium cobalticyanide*—$2K_4(Co''Cy_6) + O + H_2O = 2K_3(Co'''Cy_6) + 2KOH$. The potassium cobalticyanide is a pale yellow salt, its solution being nearly colourless, so that the brown solution formed at first when KCy in excess is added to a cobalt salt gradually becomes pale yellow when boiled in contact with air. This solution, when mixed with hydrochloric acid in excess, yields *hydro-cobalticyanic acid*, H_3CoCy_6, which is soluble, forming a distinction between cobalt and nickel. When both metals are present, the addition of HCl to the solution in excess of KCy produces a yellowish-green precipitate of *nickel cobalticyanide*, $Ni_3(CoCy_6)_2$, which is decomposed by boiling with potash, the nickel being precipitated as hydroxide, and the cobalt passing into solution as potassium cobalticyanide; $Ni_3(CoCy_6)_2 + 6KOH = 3Ni(OH)_2 + 2K_3CoCy_6$. The solution of potassium cobalticyanide is not decomposed by digestion with HgO (to precipitate the NiO), but a solution of mercurous nitrate gives a white precipitate of *mercurous cobalticyanide*, $Hg_3Co_2Cy_6$, which is converted into oxide of cobalt when heated in air.

The potassium cobalticyanide may be obtained in crystals: it is analogous to, and isomorphous with, the potassium ferricyanide, to be presently described. *Hydrocobalticyanic acid* is prepared by mixing a strong solution of the potassium-salt with sulphuric acid and alcohol, when K_2SO_4 is precipitated, and the solution yields colourless crystals of $H_6(CoCy_6)_2.H_2O$, which is a very stable and powerful acid. Potassium cobalticyanide gives, with ferrous salts, a white precipitate of *ferrous cobalticyanide*, $Fe_3(CoCy_6)_2$; and with cobalt salts a red precipitate of

cobaltous cobalticyanide, $Co''_3(Co'''Cy_6)_2.14Aq$, which loses its water at 200° C., and becomes blue.

490. **Cyanogen and iron.**—*Ferrous cyanide*, $Fe(CN)_2$, or $FeCy_2$, is obtained (apparently in combination with some KCy) as a red-brown precipitate, by adding potassium cyanide to a ferrous salt; it dissolves when boiled with an excess of the cyanide, and the solution, when evaporated, deposits yellow crystals of potassium ferrocyanide—$FeCy_2 + 4KCy = K_4FeCy_6$. This might be regarded as $4KCy.FeCy_2$, but the iron cannot be detected by any of the tests for that metal; thus, ammonium sulphide, which produces a black precipitate in ferrous salts, does not change the ferrocyanide; moreover, the K_4 may be exchanged for hydrogen or for other metals without affecting the iron and cyanogen, leading to the conclusion that the group $FeCy_6$ contains the iron in a state of intimate association with the cyanogen, so that its ordinary properties are lost. Again, the ferrocyanide is not poisonous, so that it cannot be believed to contain potassium cyanide.

Hydrogen ferrocyanide, or *hydroferrocyanic acid*, H_4FeCy_6, is prepared by mixing a cold saturated solution of potassium ferrocyanide with an equal volume of strong hydrochloric acid. It forms a white crystalline precipitate, soluble in water, but not in HCl. If it be drained, dissolved in alcohol, and ether added, it may be obtained in large crystals. It is a strong acid. When exposed to air, it absorbs oxygen, and evolves hydrocyanic acid, leaving a residue of *Prussian blue* or *ferric ferrocyanide*, $Fe_4(FeCy_6)_3$. The acid is decomposed by boiling its solution, into hydrocyanic acid and *ferrous* ferrocyanide, $Fe_2(FeCy_6)$, which is white, but becomes blue when exposed to air; $3H_4FeCy_6 = 12HCy + Fe_2(FeCy_6)$. These changes are applied to produce blue patterns in calico-printing.

Hydroferrocyanic acid is *tetrabasic*, its four atoms of hydrogen admitting of displacement by a metal to form a ferrocyanide. The group $FeCy_6$, *ferrocyanogen*, Fcy or Cfy, is a tetrad group, consisting of ferrous iron, which is diad, Fe'', and six monad cyanogen groups, (CN)', leaving four vacant bonds.

Prussian blue or *ferric ferrocyanide*, $Fe'''_4Fcy^{iv}_3$, ($Fcy = FeC_6N_6$), is prepared by adding potassium ferrocyanide to a solution of ferric chloride, or ferric sulphate; $2Fe_2Cl_6 + 3K_4Fcy = Fe_4Fcy_3 + 12KCl$. When washed and dried, it is a dark-blue amorphous body, which assumes a coppery lustre when rubbed. It cannot be obtained perfectly free from water, always retaining about 20 per cent. ($Fe_4Fcy + 12$ Aq). On heating, the water decomposes it, hydrocyanic acid and ammonia being evolved, and ferric oxide left. The water appears essential to the blue colour, for strong sulphuric acid converts it into a white powder, becoming blue again on adding water. Strong hydrochloric acid dissolves Prussian blue, forming a brown solution, which gives a blue precipitate with water. Oxalic acid dissolves it to a blue solution, used as an ink. Some ammonium salts, such as acetate and tartrate, also dissolve it. Alkalies destroy the blue colour, leaving ferric hydroxide and a solution of an alkali ferrocyanide; $Fe_4Fcy_3 + 12KOH = 2Fe_2(OH)_6 + 3K_4Fcy$. This is turned to account, in calico-printing, for producing a buff or white pattern upon a blue ground. The stuff having been dyed blue by passing, first through solution of a ferric salt, and afterwards through potassium ferrocyanide, the pattern is discharged by an alkali, which leaves the brown ferric hydroxide capable of being removed by a dilute acid, when the stuff has been rinsed, so as to leave the design white. Prussian blue is present in large quantity in many black silks, and may be extracted by heating with hydrochloric acid, and precipitating the brown solution with water.

Soluble Prussian blue, or *potassio-ferric ferrocyanide*, $K_2Fe'''_2(Fcy)^{iv}_2$, is formed when solution of ferric chloride or sulphate is poured into potassium ferrocyanide, so that the latter may be present in excess during the reaction; $Fe_2Cl_6 + 2K_4Fcy = K_2Fe_2Fcy_2 + 6KCl$. This blue is insoluble in the liquid containing saline matter

but dissolves as soon as the latter has been removed by washing. The addition of an acid or a salt re-precipitates it. By decomposing soluble Prussian blue with ferrous sulphate, a blue precipitate of *ferroso-ferric ferrocyanide*, $Fe''Fe'''_2Fcy_2$, is obtained, which is erroneously called Turnbull's blue (*ferrous ferricyanide*).

Potassio-ferrous ferrocyanide, $K_2Fe''Fcy$, is obtained as a white precipitate when a solution of ferrous salt quite free from ferric salt, such as a solution of ferrous hydrosulphite (p. 237) made by dissolving iron in H_2SO_3, is added to potassium ferrocyanide quite free from ferricyanide; $FeSO_4 + K_4Fcy = K_2SO_4 + K_2FeFcy$. The precipitate is snow-white, and remains so for some time at the bottom of the liquid, but if it be exposed to air, it eagerly absorbs oxygen and becomes blue: $6K_2FeFcy + O_3 = 3K_4Fcy + Fe_4Fcy_3 + Fe_2O_3$. Oxidising-agents, such as chlorine-water and nitric acid, change it at once into Prussian blue. When potassium ferrocyanide is added to ordinary ferrous sulphate, some Prussian blue is always formed from the ferric sulphate present in the ordinary salt. In making the Prussian blue of commerce, this precipitate is oxidised by solution of chloride of lime (p. 183), and afterwards washed with dilute HCl, to remove Fe_2O_3.

Calcium chloride gives, with potassium ferrocyanide, a white crystalline precipitate of *potassio-calcium ferrocyanide*, K_2CaFcy, which is insoluble in acetic acid, but dissolves in HCl, and is reprecipitated by ammonia. *Potassio-barium ferrocyanide*, $K_2BaFcy.3Aq$, is similar. *Manganese ferrocyanide*, Mn_2Fcy, and *zinc ferrocyanide*, Zn_2Fcy, are white precipitates. When potassium ferrocyanide is added to a zinc-salt mixed with excess of ammonia, a white crystalline precipitate of *ammonio-zinc ferrocyanide* is obtained. *Nickel ferrocyanide*, Ni_2Fcy, is a pale green precipitate. *Cobalt ferrocyanide*, Co_2Fcy, forms a pale blue-green precipitate. *Uranic ferrocyanide*, U_4Fcy_3 (?), is a rich brown-red precipitate. *Cupric ferrocyanide*, Cu_2Fcy, is also obtained as a brown-red precipitate by adding potassium ferrocyanide to cupric sulphate: it forms the colour known as *Hatchett's brown*. Its formation is a delicate test for copper, a very dilute solution giving a pink colour with the ferrocyanide.

Silver ferrocyanide, Ag_4Fcy, is obtained as a white precipitate from silver nitrate and potassium ferrocyanide: it is insoluble in dilute nitric acid, like silver chloride, but it is also insoluble in ammonia, which is the case with few silver salts. When boiled with nitric acid it is converted into the red-brown *silver ferricyanide*, which is soluble in ammonia. When silver ferrocyanide is boiled with ammonia (or KOH), it deposits metallic silver and ferric oxide, leaving silver cyanide and ammonium (or potassium) cyanide in solution—

$$2Ag_4FeCy_6 + 6NH_3 + 3H_2O = Ag_2 + Fe_2O_3 + 6AgCy + 6NH_4Cy.$$

Ferric cyanide, Fe_2Cy_6, is very unstable. When KCy is added to ferric chloride, the solution soon becomes turbid, depositing ferric hydroxide and evolving HCy; $Fe_2Cy_6 + 6H_2O = Fe_2(OH)_6 + 6HCy$.

Potassium ferricyanide, or *red prussiate of potash*, $K_3Fe'''C_6N_6$, or $3KCN.Fe'''(CN)_3$, is prepared by the action of chlorine upon potassium ferrocyanide; $K_4Fe''Cy_6 + Cl = K_3Fe'''Cy_6 + KCl$. Chlorine is passed into the solution of ferrocyanide until a little of the solution tested with ferric chloride no longer gives a blue precipitate. On the small scale, chlorine-water may be added to the ferrocyanide. The yellow colour is changed to greenish-yellow, and the solution, when evaporated and cooled, deposits dark-red prisms of the ferricyanide. It is very soluble in water, yielding a dark yellowish-green solution, but is nearly insoluble in alcohol. The aqueous solution is slowly decomposed by exposure to light, depositing a blue precipitate, and becoming partly converted into ferrocyanide. If the solution be mixed with acetic acid, and heated, it deposits a blue precipitate, a reaction which is turned to account in dyeing. An alkaline solution of potassium ferricyanide acts as a powerful oxidising-agent, becoming reduced to ferrocyanide; $2K_3Fe'''Cy_6 + 2KOH = 2K_4Fe''Cy_6 + H_2O + O$. Such a solution converts chromic oxide into potassium chromate, and bleaches indigo, whence it is used as a *discharge* in calico-printing, for white patterns on an indigo

ground. Potassium ferricyanide is also reduced to ferrocyanide when boiled with potassium cyanide—

$$2K_3Fe'''Cy_6 + 2KCN + 2H_2O = 2K_4Fe''Cy_6 + HCN + NH_3 + CO_2.$$

Hydrogen ferricyanide, or *hydroferricyanic acid*, $H_3Fe'''Cy_6$, is obtained by decomposing lead ferricyanide with H_2SO_4, not in excess. It may be crystallised in brown needles by evaporation *in vacuo*. Its solution is decomposed by boiling, with evolution of HCy and separation of a blue precipitate. Hydroferricyanic acid is tribasic, the 3 atoms of hydrogen being displaced by metals to form ferricyanides.

Ferrous ferricyanide, or *Turnbull's blue*, $Fe''_3Fe'''_2Cy_{12}$.—Whilst potassium ferrocyanide gives a light blue precipitate with common $FeSO_4$, the ferricyanide gives a dark blue precipitate, resembling Prussian blue. This contains the same proportions of iron and cyanogen as the ferroso-ferric ferrocyanide, $Fe''Fe'''_2(Fe''Cy_6)_2$, and it is sometimes regarded as identical with it, on the supposition that the ferrous sulphate reduces the ferricyanide to ferrocyanide. Ferric salts give no precipitate with the ferricyanide, but only a dark brown solution, probably containing ferric ferricyanide, which yields a blue precipitate of ferrous ferricyanide with reducing-agents such as H_2SO_3, and is used as a test.

Lead ferricyanide, $Pb_3Fe_2Cy_{12}.16Aq$, is deposited in red-brown crystals on mixing strong solutions of lead nitrate and potassium ferricyanide. *Silver ferricyanide*, $Ag_6Fe_2Cy_{12}$, has been already mentioned as a red-brown precipitate formed by boiling the ferrocyanide with dilute nitric acid. Cold potash converts it into black Ag_2O and potassium ferricyanide; on boiling, the black changes to pink; $3Ag_2O + K_6Fe_2Cy_{12} = 6AgCy + 6KCy + Fe_2O_3$. The pink precipitate is a compound of AgCy with silver ferricyanide, which may also be obtained by boiling silver ferricyanide with silver oxide; $Ag_6Fe_2Cy_{12} + 3Ag_2O = Fe_2O_3 + 12AgCy$, which combines with undecomposed silver ferricyanide. On continuing to boil the silver ferricyanide with potash, the pink precipitate again becomes black, for the potassium cyanide reduces the silver ferricyanide to ferrocyanide, which is ultimately decomposed by the silver oxide, with separation of metallic silver—

(1) $2Ag_6Fe_2Cy_{12} + 4KCN + 4H_2O = 3Ag_4FeCy_6 + K_4FeCy_6 + 2HCN + 2CO_2 + 2NH_3$;
(2) $4Ag_4FeCy_6 + 2Ag_2O = Ag_6Fe_2Cy_{12} + 12AgCy + 2FeO + Ag_2$.

In the preparation of K_3FeCy_6, if an excess of chlorine be employed, the liquid when evaporated deposits a precipitate of *Prussian green*, which appears to be a compound of ferric ferrocyanide and ferricyanide, $2Fe_4Fcy_3.FeFcy$, for, when boiled with potash, it yields 5 molecules of ferric hydroxide, 3 molecules of potassium ferrocyanide, and 1 molecule of potassium ferricyanide.

491. **Nitroprussides.**—When potassium ferricyanide is acted on by a mixture of $NaNO_2$ and acetic acid, it is converted into potassium nitroprusside, $K_4Fe_2Cy_{10}(NO)_2$, probably according to the equation—

$$K_6Fe_2Cy_{12} + 4HNO_2 = K_4Fe_2Cy_{10}(NO)_2 + 2HCy + H_2O + KNO_3 + KNO_2.$$

If $HgCl_2$ be added to the solution, $HgCy_2$ crystallises, and, on further evaporation, red prisms of sodium nitroprusside are deposited—

$$K_6Fe_2Cy_{12} + 4NaNO_2 + 2H\bar{A} + HgCl_2 =$$
$$Na_4Fe_2Cy_{10}(NO)_2 + HgCy_2 + 2KCl + 2K\bar{A} + KNO_2 + KNO_3 + H_2O.$$

Sodium nitroprusside, $Na_4Fe_2Cy_{10}(NO)_2.4Aq$, is prepared by a process founded upon the above reactions (Hadow).

332 grains of potassium ferricyanide are dissolved in half a pint of boiling water and 800 grains of acetic acid are added. Into this hot solution is poured a cold solution containing 80 grains of sodium nitrite and 164 grains of mercuric chloride in half a pint of water. The solution is kept at 60° C. for some hours, until a little no longer gives a blue coloration with ferrous sulphate (a little more sodium nitrite and acetic acid may be added if necessary). The mixture is then boiled down till it solidifies to a thick paste on cooling; this is squeezed in linen to drain off the solution of potassium acetate; the mass is dissolved in boiling water, and allowed to cool, when most of the mercuric cyanide crystallises. On concentrating the red filtrate, and cooling, crystals of sodium nitroprusside are obtained, and may be purified by recrystallisation.

Sodium nitroprusside was originally prepared by boiling ferrocyanide with nitric acid (Playfair). Potassium ferrocyanide, in powder, is dissolved in twice its weight of strong HNO_3 (1.42) mixed with an equal volume of water; effervescence occurs, from escape of CO_2 and N, and the odours of $(CN)_2$, HCN and cyanic acid may be distinguished. When the salt has dissolved, the solution is heated on a steam bath till it no longer gives a blue with $FeSO_4$. It is then allowed to cool, when KNO_3 crystallises, and the solution is boiled with excess of Na_2CO_3 and filtered; the filtrate when evaporated deposits crystals of nitroprusside.

Sodium nitroprusside is very soluble in water; the solution deposits a blue precipitate when exposed to light. When its solution is rendered alkaline by soda, and boiled, the NO group exerts a reducing action, ferrous hydroxide being precipitated, and sodium ferrocyanide and nitrite remaining in solution. Alkali sulphides have also a reducing effect upon the solution, producing a fugitive violet-blue colour, even in very weak solutions, rendering sodium nitroprusside a most delicate test for sulphur in organic compounds, which yield sodium sulphide when fused with sodium carbonate. The sulphur in an inch of human hair may be detected by this test. The higher (yellow) alkali sulphides should be reduced by warming with KCN solution. Alcoholic solutions of nitroprusside and sulphide of sodium yield a purple oily compound soon decomposing into ammonia and several cyanogen compounds.

With silver nitrate, sodium nitroprusside gives a buff precipitate of *silver nitroprusside*, $Ag_4Fe_2Cy_{10}(NO)_2$, and by decomposing this with HCl the *hydronitroprussic acid*, $H_4Fe_2Cy_{10}(NO)_2$, may be obtained, by evaporation, *in vacuo*, in red deliquescent prisms (with $1H_2O$). It is very unstable.

Potassium carbonyl ferrocyanide, $K_3FeCOCy_5$ is obtained by heating a solution of K_4FeCy_6 with CO.

492. *Chromic cyanide*, Cr_2Cy_6, is a pale green precipitate produced by KCy with chrome alum; heated with excess of KCy, it yields *potassium chromicyanide*, $K_6Cr_2Cy_{12}$, which may be obtained in yellow prisms.

Manganous cyanide, $MnCy_2$, is probably contained in the greenish precipitate by KCy in manganous acetate; an excess of KCy dissolves it to a colourless solution, from which alcohol separates blue crystals of *potassium manganocyanide*, $K_4MnCy_6.3Aq$, isomorphous with the ferrocyanide. When exposed to air, the solution of the manganocyanide absorbs oxygen, and deposits red prisms of *potassium manganicyanide*, $K_6Mn_2Cy_{12}$, isomorphous with the ferricyanide.

Cuprous cyanide, Cu_2Cy_2, is obtained as a white precipitate by boiling cupric sulphate with KCy, when *cupric cyanide*, $CuCy_2$, is first formed as a brown precipitate, which evolves cyanogen when boiled. Cuprous cyanide dissolves in KCy, and the solution yields colourless crystals of *potassium cupro-cyanide*, $K_2Cu'_2Cy_4$, which gives a precipitate of *plumbic cupro-cyanide*, $PbCu_2Cy_4$, with lead acetate. By decomposing the lead salt with H_2S, a solution of the corresponding acid, $H_2Cu_2Cy_4$, is obtained, but this soon decomposes into 2HCy and Cu_2Cy_2.

493. **Silver cyanide**, AgCy, is obtained as a white precipitate when hydrocyanic acid or a cyanide is added to silver nitrate. Its insolubility in water renders its formation a very delicate test for HCy (in the absence of other acids forming insoluble silver salts) and an accurate method of estimating its quantity.

Silver cyanide is not altered by sunlight like silver chloride, and is dissolved when boiled with strong nitric acid, which does not dissolve the chloride. The nitric solution, when cooled, deposits flocculent masses of minute needles of the composition $AgCy.2AgNO_3$, which detonate when heated.

Silver cyanide, when heated, fuses, evolves cyanogen, and leaves a residue of silver mixed with *silver paracyanide*, AgC_3N_3. Silver cyanide dissolves in ammonia like the chloride, but the latter is deposited in microscopic octahedra, while the cyanide forms distinct needles; a mass of silver cyanide, moistened with ammonia and warmed, becomes converted into needles. Potassium hydroxide does not decompose silver cyanide. Potassium cyanide readily dissolves silver cyanide, forming $KAgCy_2$, which may be crystallised in six-sided tables. It is used in electro-plating.

Mercuric cyanide, $HgCy_2$, is prepared by dissolving precipitated HgO in excess of solution of HCN, and evaporating, when the cyanide is deposited in four-sided prisms, which dissolve in eight parts of cold water, and are insoluble in alcohol. For its behaviour when heated see p. 687. It is one of the most stable of the cyanides, scarcely allowing the cyanogen to be detected by the ordinary tests. Dilute H_2SO_4 and HNO_3 do not decompose it, but HCl liberates HCy. KOH and NH_3 do not precipitate its solution.

Mercuric cyanide dissolves mercuric oxide when boiled, giving an alkaline solution, which deposits needles of *mercuric oxycyanide*, Hg_2OCy_2. When solutions of mercuric cyanide and silver nitrate are mixed, the solution becomes acid, and, on stirring, deposits fine needles containing $Ag.Hg.NO_3.Cy_2.2Aq$. The acid reaction of the solution proves that some of the mercuric cyanide has become converted into mercuric nitrate; the same salt may be obtained by dissolving silver cyanide in mercuric nitrate. Neither mercuric cyanide nor silver nitrate is precipitated by excess of ammonia, but a mixture of the two salts gives an abundant precipitate, containing $HgCy_2.7AgCy.2HgO$, which explodes when heated. The crystalline salt is probably $AgCy.CyHgNO_3.2Aq$, containing $HgCy_2$, in which NO_3 is substituted for Cy. Other crystalline compounds of the same kind are formed by $HgCy_2$; such as NaCy.CyHgCl and KCy.CyHgI. A potassio-mercuric cyanide, KCy.CyHgCy.CyK, may be obtained in fine crystals, which may be decomposed by mercuric chloride, yielding $HgCl_2.HgCy_2$ or Hg″Cy′Cl′.

Mercuric cyanide was originally prepared by Scheele, when he discovered that prussic acid could be prepared from Prussian blue. This was boiled with mercuric oxide and water till the blue colour had disappeared; $Fe_4(Cy_6Fe)_3 + 9HgO = 9HgCy_2 + 2Fe_2O_3 + 3FeO$. The filtered solution was mixed with sulphuric acid, shaken with iron filings, which precipitated the mercury, and distilled to obtain hydrocyanic acid; $HgCy_2 + H_2SO_4 + Fe = 2HCy + FeSO_4 + Hg$.

Mercuric cyanide may be directly obtained from potassium ferrocyanide by boiling it with mercuric sulphate (2 parts) and water (8 parts)—

$$2K_4FeCy_6 + 7HgSO_4 = 6HgCy_2 + 4K_2SO_4 + Fe_2(SO_4)_3 + Hg.$$

The mercurous cyanide is not known; when mercurous nitrate is decomposed by potassium cyanide, a solution of mercuric cyanide is formed, and metallic mercury is precipitated; $Hg_2(NO_3)_2 + 2KCy = HgCy_2 + Hg + 2KNO_3$.

Gold cyanides.—*Potassium aurocyanide*, $2KAu'Cy_2$, is obtained by dissolving gold in KCN solution (p. 514), or by dissolving *fulminating gold* (p. 518) in hot water containing pure potassium cyanide. The filtered solution deposits colourless crystals of the aurocyanide, which are very soluble in hot water. *Aurous cyanide*, AuCy, is obtained as a crystalline precipitate by adding HCl to solution of the aurocyanide of potassium.

Potassium auricyanide, $KAu'''Cy_4$, is prepared by mixing hot strong solutions of gold trichloride and potassium cyanide. It forms colourless tables (with $1H_2O$). With $AgNO_3$ a precipitate of *silver auricyanide*, $AgAuCy_4$, is obtained, and if this be treated with HCl, avoiding excess, the silver is precipitated as AgCl, and the solution, evaporated *in vacuo*, yields crystals of *auric cyanide*, $AuCy_3.3Aq$.

Both aurocyanide and auricyanide of potassium are used in electro-gilding.

494. **Platinum cyanides.**—The cyanides of platinum have not been prepared in a pure state, but the salts known as *platinocyanides* exceed the ferrocyanides in the force with which they retain the platinum disguised to the ordinary tests. When KCN is strongly heated on platinum foil, the metal is attacked, and an orange-coloured mass is produced. Spongy platinum is slowly dissolved by a boiling solution of KCN, and if mixed with the solid cyanide, and heated to 600° C. in steam, *potassium platinocyanide* is formed—

$$Pt + 4KCy + 2H_2O = K_2Pt''Cy_4 + 2KOH + H_2.$$

When solutions of potassium cyanide and platinic chloride are boiled together till colourless, the platinocyanide is found in solution—

$$PtCl_4 + 6KCN + 4H_2O = K_2Pt(CN)_4 + 4KCl + 2NH_3 + H_2C_2O_4.$$

Or the ammonio-platinic chloride may be boiled with potash and a strong solution of potassium cyanide until no more ammonia is evolved.

Potassium platinocyanide is also prepared by dissolving platinous chloride in solution of potassium cyanide; $PtCl_2 + 4KCy = K_2PtCy_4 + 2KCl$. It crystallises in prisms (with $3H_2O$), which are yellow by transmitted light, and reflect a blue colour. They are very soluble in water. The solution is colourless, and gives a

characteristic blue precipitate with mercurous nitrate. $CuSO_4$ also gives a blue precipitate, and if this be decomposed by aqueous H_2S, it yields a solution of *hydroplatinocyanic acid*, H_2PtCy_4, which crystallises from ether in red prisms (with $5H_2O$) with a blue reflection.

Barium platinocyanide, $BaPtCy_4.4Aq$, is prepared by decomposing the cupric salt with baryta. It is dichroic, being green when looked at along the primary axis of the crystal, and yellow across it. It is remarkable for its property of becoming luminous when exposed to the Röntgen rays, in which respect it resembles, but excels, many other platinocyanides.

Magnesium platinocyanide, $MgPtCy_4.7Aq$, obtained by decomposing the barium salt with $MgSO_4$, crystallises in large prisms, deep red by transmitted light, but when viewed by reflected light, the sides of the prisms exhibit a brilliant beetle-green, and the ends a deep blue or purple colour. When the red salt is gently warmed, even under water, it becomes bright yellow, from production of $MgPtCy_4.6Aq$, which may be obtained in crystals from the solution at 71° C. Heated at 100° C., the yellow salt becomes white $MgPtCy_4.2Aq$, and at about 180° C. it again becomes yellow, and is then anhydrous. If a little of the yellow anhydrous salt be placed on the powdered red salt (with 7Aq), it abstracts water from it, and converts it into the yellow salt with 6Aq, while it is itself changed to the white salt with 2Aq, so that a white layer is formed between two yellow layers. The yellow salt may also be obtained by crystallisation from alcohol.

When the platinocyanides are attacked, in solution, by oxidising-agents, such as chlorine, bromine, or nitric acid, new salts are formed, which have a coppery lustre, and act as oxidising-agents in alkaline solutions, like the ferricyanides. These were formerly called *platinicyanides*, but were shown by Hadow to contain chloro-, bromo-, &c., platinocyanides. When chlorine is passed into a hot solution of potassium platinocyanide, it deposits, on evaporation, colourless crystals of the chloroplatinocyanide, $K_2PtCy_4Cl_2.2Aq$. When these are treated with a strong solution of the platinocyanide, they are converted into copper-red needles of $5K_2PtCy_4.K_2PtCy_4Cl_2.3H_2O.18Aq$. This compound, when boiled with potash, yields the platinocyanide and potassium hypochlorite—

$$5K_2PtCy_4.K_2PtCy_4Cl_2 + 2KOH = 6K_2PtCy_4 + KOCl + KCl + H_2O.$$

495. **Cyanogen Halides.**—*Cyanogen chloride*, C ⋮ N·Cl, is prepared by the action of chlorine upon moist mercuric cyanide, in the dark: $HgCy_2 + 2Cl_2 = HgCl_2 + 2CyCl$. On gently heating, the cyanogen chloride passes off in vapour, and may be condensed in a tube surrounded with a freezing-mixture. It is a colourless liquid, boiling at 15° C., and yielding a vapour which irritates the eyes, causing tears. When exposed to light, or treated with acids, it polymerises into *cyanuric chloride*, Cy_3Cl_3, which fuses at 146° and boils at 190° C. This has also an irritating effect on the eyes. It is sparingly soluble in cold water, and is decomposed by boiling water, yielding cyanuric acid: $Cy_3Cl_3 + 3H_2O = Cy_3(OH)_3 + 3HCl$. Both these chlorides may be obtained by the action of chlorine on hydrocyanic acid.

In practice cyanogen chloride is generally required in solution which is best prepared by dissolving 260 grams of KCN and 90 grams of crystallised $ZnSO_4$ in 8 litres of water, and passing Cl until the $ZnCy_2$ at first thrown down is nearly redissolved.

Cyanogen bromide, CyBr, is obtained in crystals, mixed with KBr, when bromine is gradually added to a strong well-cooled solution of KCy. On gently heating, it sublimes in crystals, which are very volatile and cause tears. When heated in a sealed tube, it becomes Cy_3Br_3. It melts at 52° C. and boils at 61° C.

Cyanogen iodide, CyI, is prepared by dissolving iodine in a warm strong solution of KCy, when a crystalline mass of KI and CyI is obtained on cooling, from which the CyI may be extracted by gently heating or by treatment with ether. It crystallises easily in colourless needles or tables, which are sparingly soluble in water, very volatile, and have a tear-exciting odour. It sometimes occurs in commercial iodine, from which it may be sublimed in a tube or flask plunged in boiling water. When heated to 100° C., in a sealed tube, with alcoholic ammonia, it yields hydriodide of guanidine, $CNI + 2NH_3 = CN_3H_5.HI$.

496. **Cyanides of Hydrocarbon Radicles, or Acid Nitriles.**—The term *nitrile* was originally applied to the final product of the removal of water from an ammonium salt (*cf.* p. 667), the amide being the intermediate product. Thus, when the group $C\begin{matrix}O\\ \diagup\\ \diagdown\\ ONH_4\end{matrix}$, characteristic of the organic ammonium salts, loses 1 mol. H_2O, it passes into the $C\begin{matrix}O\\ \diagup\\ \diagdown\\ NH_2\end{matrix}$ group of the amides, and when this loses 1 mol. H_2O, it becomes $C{\equiv}N$, the nitrile group. It was later found that the nitriles are identical with the cyanides of the hydrocarbon radicles.

Hence there are two general lines on which these compounds may be prepared, viz., (1) by reactions which produce cyanides, such as (*a*) by heating the iodide of a hydrocarbon radicle with KCN in alcoholic solution, $CH_3I + KCN = KI + CH_3{\cdot}CN$, or (*b*) by distilling an alkali alkyl sulphate with KCN, $KCH_3SO_4 + KCN = CH_3{\cdot}CN + K_2SO_4$; (2) by dehydrating ammonium salts or amides by distillation with P_2O_5, $CH_3{\cdot}CONH_2 - H_2O = CH_3{\cdot}CN$.

The ease with which the CN group reverts to the COOH group when the cyanides or nitriles are hydrolysed and the importance thus attaching to these compounds in synthetic chemistry have been dwelt upon already (p. 688). When an acid is the hydrolytic agent the ammonium salt is produced $CH_3{\cdot}CN + 2HOH = CH_3{\cdot}COONH_4$; but when it is an alkali the NH_3 is evolved, $CH_3{\cdot}CN + HOH + KOH = NH_3 + CH_3{\cdot}COOK$. The reaction shows that of two possible formulæ for the cyanide, $H_3C{\cdot}C \vdots N$ and $H_3C{\cdot}N \vdots C$, the former must be correct, since the hydrolysis does not part the C atoms, which must therefore be directly united in the cyanide. The action of nascent hydrogen on the cyanide confirms this, for an amine is produced—$CH_3{\cdot}CN + H_4 = H_3C{\cdot}C\begin{matrix}H_2\\ \diagup\\ \diagdown\\ NH_2\end{matrix}$.

Cyanogen itself is *oxalonitrile*, and may be obtained by dehydrating ammonium oxalate $COONH_4{\cdot}COONH_4 = CN{\cdot}CN + 4H_2O$. Hydrocyanic acid is *formonitrile*, obtained from ammonium formate; $HCOONH_4 = HCN + 2H_2O$.

Methyl cyanide, or *acetonitrile*, $CH_3{\cdot}CN$, prepared as above, is a volatile liquid of pleasant odour boiling at 81°.6 C. Its sp. gr. is 0.8, and it is soluble in water and alcohol.

The tendency for the nitrogen in the C ⋮ N group to become pentavalent, leads to the formation of crystalline compounds of CH_3CN with Br_2, HBr and HI, &c. Certain chlorides also combine with methyl cyanide to form crystalline volatile substances, decomposed by water; such compounds are formed with PCl_5, $SbCl_5$, and $SnCl_4$. When methyl cyanide is acted on by sodium, part of it is decomposed with violent evolution of methyl hydride, and the remainder is polymerised to form *cyanmethine* $(CH_3)_3(CN)_3$, an organic base, soluble in water, and having a very bitter taste. It forms prismatic crystals, which may be sublimed.

An instructive reaction yielding methyl cyanide is that between diazomethane and HCN; $CH_2 : N_2 + HCN = CH_3CN + N_2$. This illustrates the application of diazomethane in the formation of a number of organic compounds.

Methyl cyanide is present, in small quantity, in coal-naphtha, and in the distillate from beet-sugar refuse.

Ethyl cyanide, or *propio-nitrile*, $C_2H_5{\cdot}CN$, is similarly obtained. It resembles methyl cyanide, except in being less soluble in water, and in boiling at 98° C. It

combines with HCl to form a sparingly soluble crystalline compound, which absorbs water from the air, and yields propionic acid and ammonium chloride.

Sodium acts on ethyl cyanide in the same way as on $CH_3{\cdot}CN$: one part is decomposed, with evolution of butane (di-ethyl)—$2C_2H_5CN + Na_2 = C_4H_{10} + 2NaCN$. The remainder is polymerised to *cyanethine* $(C_2H_5)_3(CN)_3$.

Phenyl cyanide, or *benzonitrile*, $C_6H_5{\cdot}CN$, also called *cyanobenzene*, may be prepared by dehydrating ammonium benzonate, also by distilling potassium benzenesulphonate with KCN (or well-dried K_4FeCy_6); $C_6H_5{\cdot}SO_2K + KCN = C_6H_5{\cdot}CN + K_2SO_3$. It is a colourless liquid smelling of bitter almonds; sp. gr. 1.023, boiling at 191° C. By hydrolysis it becomes ammonium benzoate. Nascent hydrogen converts it into *benzylamine*, $C_6H_5CH_2{\cdot}NH_2$. Its formation from diazobenzene has already been noticed (p. 681).

Benzyl cyanide, $C_6H_5{\cdot}CH_2{\cdot}CN$, or *phenyl-acetonitrile*, is obtained by heating benzyl chloride with potassium cyanide and alcohol. It occurs in the essentail oils of nasturtium and cress. When boiled with alkalies, it yields ammonia and *phenyl acetic* (or *α-toluic*) *acid*, $C_6H_5{\cdot}CH_2{\cdot}CO_2H$.

497. **Isocyanides, Isonitriles, or Carbylamines (Carbamines).**—These compounds are isomeric with the cyanides of the hydrocarbon radicles, but differ from them in being much less easily attacked by alkalies and in yielding formic acid and an amine of the hydrocarbon radicle when hydrolysed by acids, methyl isocyanide, for example, yielding methylamine, $H_3C{\cdot}NH_2$, and formic acid, HCOOH. This reaction shows that the C atoms in the isocyanide are not united directly, but through the N atom; in other words, the second of the two possible formulæ given above for the cyanide, $H_3C{\cdot}N \vdots C$, must be ascribed to the isocyanide.* The formation of *two* carbon compounds on hydrolysis is easily explained on this assumption; $CH_3{\cdot}NC + 2HOH = CH_3{\cdot}NH_2 + HCOOH$.

The isocyanides are obtained in small proportion together with the cyanides when the iodides of the hydrocarbon radicles are heated with KCN, but they are almost the sole products when AgCN is substituted for the KCN. The iodide and AgCN are heated in a sealed tube with ether at 140° C., when a crystalline compound of the isocyanide with AgCN is formed; this is distilled with water and KCN, whereupon the isocyanide distils; $CH_3I + 2AgCN = CH_3{\cdot}NC,AgCN + AgI$;

$$CH_3{\cdot}NC,AgCN + KCN = CH_3{\cdot}NC + KCN,AgCN.$$

The term *carbamine* refers to the idea formerly entertained that the isocyanides were *amines* in which carbon is substituted for hydrogen; thus, methyl carbamine, $NC{\cdot}CH_3$, might be regarded as methylamine, NH_2CH_3, in which C″ is substituted for H_2. Their connection with the amines is illustrated by the fact that they can be prepared by the *action of chloroform and alcoholic potash on the amines; e.g.*, $CH_3{\cdot}NH_2 + CHCl_3 + 3KOH = CH_3{\cdot}NC + 3KCl + 3HOH$.

The isocyanides often accompany the cyanides of the alcohol-radicles, especially when prepared by distilling the acid ethereal salts, such as potassium ethylsulphate, with potassium cyanide. For this reason the cyanides of alcohol-radicles were formerly described as having an offensive smell, which is really characteristic of the isocyanides mixed with them.

Methyl isocyanide or *methyl carbamine*, $H_3C{\cdot}NC$, is prepared as described above. It is lighter than water (sp. gr. 0.76) and moderately soluble in it. It has an extremely unwholesome smell, and boils at 59° C. Methyl carbamine is slightly alkaline; it combines with HCl gas, forming a crystalline hydrochloride, which is decomposed by water into formic acid and methylamine hydrochloride; $H_3C{\cdot}NC.HCl + 2H_2O = H_3C{\cdot}NH_2{\cdot}HCl + HCO_2H$.

* According to Nef the isocyanides must be regarded as containing bivalent carbon, $H_3C{\cdot}N{:}C$.

Ethyl isocyanide, or *ethyl carbamine*, $H_5C_2{\cdot}NC$, prepared like the methyl compound, boils at 79° C., and has a repulsive odour like that of hemlock. It is lighter than water, and slightly alkaline. When heated with water at 180° C. for some hours it is converted into ethylamine formate ;

$$H_5C_2{\cdot}NC + 2H_2O = H_5C_2{\cdot}NH_2{\cdot}HCO_2H.$$

Heated alone, in a sealed tube, at 230° C., it is metamerised into propionitrile ; $H_5C_2{\cdot}NC = H_5C_2{\cdot}CN$. Ethyl carbamine forms a crystalline salt with HCl, from which very strong, well cooled potash separates an oily layer of *ethyl formamide ;* $CN{\cdot}C_2H_5 + H_2O = HCO{\cdot}NHC_2H_5$. Glacial acetic acid also converts ethyl carbamine into ethyl formamide, producing acetic anhydride and much heat—

$$CN{\cdot}C_2H_5 + 2(C_2H_3O{\cdot}OH) = HCO{\cdot}NHC_2H_5 + (C_2H_3O)_2O.$$

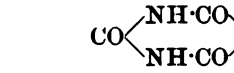
Phenyl isocyanide, or *phenyl carbamine*, $H_5C_6{\cdot}NC$, is prepared by mixing aniline with a saturated alcoholic solution of potash, and gradually adding chloroform ; the distillate is treated with oxalic acid to remove aniline, with potash to remove water, and re-distilled. Phenyl carbamine has a very terrible odour ; it is green by transmitted light, and shows a blue reflection. It begins to boil at 166° C., but soon decomposes, being converted, at 230° C., into an odourless liquid which crystallises on cooling. When heated, in a sealed tube, at 200° C., phenyl carbamine slowly metamerises into phenyl cyanide, or benzonitrile, $H_5C_6{\cdot}CN$. Treated with acids, it yields formic acid and salts of phenylamine (aniline) ; $H_5C_6{\cdot}NC + 2H_2O = H_5C_6{\cdot}NH_2 + HCO_2H$.

498. *Tautomerism.*—It has been seen that the cyanides of alcohol-radicles exist in two forms, as though they were derived from two hydrocyanic acids, $H{\cdot}C{\equiv}N$ and $H{\cdot}N{\equiv}C$. It will be seen later that derivatives of cyanamide also appear to be derived from two isomerides, $H_2N{\cdot}C{\vdots}N$ and $HN:C:NH$. Two hydrocyanic acids or two cyanamides, however, have never been prepared. It is the case with a large number of substances that, although they do not exist in isomeric forms, they behave in different reactions as if they had two structural formulæ, either of which could be assumed according to the conditions. Such compounds are said to possess *tautomeric* structures. The derivatives of one form (the *stable* form) are generally more stable than those of the other (the *labile* form or *pseudoform*).

Tautomerism is generally connected with the migration of a H atom, as will be seen from the above examples. It is very common among ketonic compounds, in which the grouping $\cdot CH:COH\cdot$ occurs, this tending to become $\cdot CH_2{\cdot}CO\cdot$ (*cf.* ethyl acetoacetate, p. 643) ; the former is the *hydroxyl-* or *enol-* form, while the latter is the *keto-* form. *Cf.* also *lactams* and *lactims* (pp. 674, 679), and *amidines* (p. 698).

From the fact that the chief product of the action of CH_3I on KCN is methyl cyanide, it may be supposed that potassium cyanide is a salt of $H{\cdot}C{\vdots}N$. Silver cyanide, on the other hand, must be a salt of $H{\cdot}N{\vdots}C$, for the chief product of its reaction with methyl iodide is methyl isocyanide.

499. **Hydroxy- and Thio-Cyanogen Compounds.—Cyanuric acid**, $Cy_3(OH)_3$, is obtained by heating urea till the melted mass solidifies ; $3CO(NH_2)_2 = 3NH_3 + (CN)_3(OH)_3$. The residue is washed with water, dissolved in KOH, and the cyanuric acid precipitated by adding HCl. A better yield is obtained by passing dry chlorine over urea kept in fusion by a gentle heat—$3CO(NH_2)_2 + Cl_3 = 2NH_4Cl + HCl + N + (CN)_3(OH)_3$. The residue is washed with cold water, and crystallised from hot water. Cyanuric acid crystallises in prisms containing 2Aq. It is insoluble in alcohol. It is a tribasic acid. It is probable that cyanuric acid is a closed-chain compound, and it may be represented by either of the tautomeric formulæ $C(OH)\langle^{N{\cdot}C(OH)}_{N:C(OH)}\rangle N$, or


, derivatives (the cyanuric esters, *e.g.*, $C_3N_3O_3(CH_3)_3$) of both forms being known.

Trisodium cyanurate, $(CN)_3(ONa)_3$, is insoluble in hot solution of soda and forms a crystalline precipitate on heating solution of cyanuric acid mixed with excess of soda. *Barium cyanurate*, Cy_3O_3HBa, is obtained as a crystalline precipitate by dissolving cyanuric acid in NH_3, and stirring with $BaCl_2$. It has a great tendency to deposit on the lines of friction by the stirring-rod. The most characteristic test for cyanuric acid is ammoniacal $CuSO_4$, which gives a violet crystalline precipitate containing $Cy_6(OH)_4 \cdot O_2 \cdot Cu(NH_3)_2$. *Silver cyanurate*, $Cy_3(OAg)_3$ is obtained as a crystalline precipitate by adding ammonium cyanurate to silver nitrate.

500. **Cyanic acid**, CyOH, is prepared by distilling cyanuric acid (dried at 100° C.), and condensing in a receiver surrounded by a freezing-mixture; $Cy_3(OH)_3 = 3CyOH$. The cyanic acid is a colourless liquid, of sp. gr. 1.14 at 0° C., which smells rather like acetic acid. It cannot be kept, for when the receiver is taken out of the freezing-mixture the acid becomes turbid, and presently begins to boil explosively, being entirely converted in a few minutes into a white hard solid, known as *cyamelide*, which is a polymeride of cyanic acid, into which it is reconverted by distillation. When cyanic acid is mixed with water, heat is evolved, and the liquid becomes alkaline; $CN \cdot OH + 2H_2O = NH_4 \cdot HCO_3$. A compound of HCl and CNOH is obtained as a fuming liquid by acting on a cyanate with dry HCl gas.

It is doubtful whether cyanic acid is HO·C ⋮ N (the nitrile of carbonic acid) or HN : C : O (*carbimide*). The former would be cyanic acid and the latter isocyanic acid. At one time it was supposed that derivatives of both were known, but the compounds formerly called esters of cyanic acid have been shown to have a different constitution.

Potassium cyanate.—The compound formerly so called is probably the *isocyanate*, K·N : C : O, since it has been found to give rise to alkyl isocyanates when heated with potassium alkyl sulphates. It is formed when the cyanide is oxidised by fusion in contact with air or with metallic oxides.

It may be prepared by oxidising potassium ferrocyanide with potassium dichromate. Four parts of perfectly dried K_4FeCy_6 are intimately mixed with 3 parts of $K_2Cr_2O_7$; the mixture is thrown, in small portions, into a porcelain or iron dish, heated sufficiently to kindle it. When the whole has smouldered and blackened, it is allowed to cool, introduced into a flask, boiled with strong alcohol, and filtered hot; the isocyanate crystallises out on cooling, and the mother liquor may be employed to extract a fresh portion.

Potassium isocyanate is also prepared by passing cyanogen chloride into well-cooled potash; $CN \cdot Cl + 2KOH = KCNO + KCl + H_2O$. It crystallises in plates; it is decomposed by moist air into $KHCO_3$ and ammonia; $K \cdot NC : O + 2H_2O = KHCO_3 + NH_3$. It is very soluble in water, but the solution soon decomposes, especially if heated—$2K \cdot NC : O + 4H_2O = CO(OK)_2 + CO(ONH_4)_2$. If the freshly prepared solution be mixed with dilute acetic acid, a crystalline precipitate of potassium dihydrogen cyanurate is obtained; $3\ KNCO + 2HA = KH_2C_3N_3O_3 + 2KA$. Solution of potassium isocyanate effervesces with acids evolving CO_2, together with some pungent vapour of cyanic (or isocyanic) acid, and leaving an ammonium salt in solution.

Ammonium cyanate, $NH_4 \cdot O \cdot CN$, or $O : C : N(NH_4)$ is prepared by

mixing vapour of cyanic acid with ammonia gas in excess, when it is deposited in minute crystals, which effervesce with acids, evolving CO_2. The cyanate or isocyanate is also formed when potassium isocyanate is decomposed by ammonium sulphate. By employing strong solutions and cooling artificially, the bulk of the potassium sulphate may be crystallised out. The isocyanate has not been crystallised, for, when its solution is evaporated, it metamerises into urea; $NH_4 \cdot NC:O = (NH_2)_2CO$ (p. 670).

501. **Thiocyanic acid, HSCN (*sulphocyanic*)**, is obtained by decomposing mercuric thiocyanate with hydrogen sulphide. It is a colourless pungent liquid, boiling below 100° C., being then decomposed into hydrocyanic and *persulphocyanic* acids; $3CySH = HCy + Cy_2S_3H_2$. It mixes with water, but the solution soon decomposes—

$$3HSCN + 6H_2O = CS_2 + H_2S + NH_4HCO_3 + (NH_4)_2CO_3.$$

Thiocyanic acid and the thiocyanates give an intense blood-red colour with ferric salts, producing ferric thiocyanate; the red is bleached by $HgCl_2$, which distinguishes it from ferric acetate and meconate.

Potassium thiocyanate, or *sulphocyanide*, KCSN, may be obtained by direct fusion of potassium cyanide with sulphur, or by boiling sulphur with solution of the cyanide.

It is best prepared by fusing dried potassium ferrocyanide (3 parts), potassium carbonate (1 part), and sulphur (2 parts), at a low red heat, in a clay crucible. The cooled mass is extracted by hot water, evaporated, and the residue boiled with alcohol, which deposits the thiocyanate on cooling. KCy is formed by the reaction between the ferrocyanide and the carbonate (p. 691), and combines with the sulphur.

Potassium thiocyanate forms prismatic crystals, which are deliquescent and very soluble in water, producing great reduction of temperature. It fuses easily, becoming a dark blue colour, which fades on cooling; it burns when heated in air, potassium sulphate being produced. When hydrochloric acid is added to a strong solution of potassium thiocyanate, a yellow precipitate of persulphocyanic acid is obtained; this may be crystallised from hot water, and yields a yellow precipitate of *lead persulphocyanate*, $PbCy_2S_3$, with lead nitrate. When heated with sulphuric acid mixed with an equal volume of water, potassium thiocyanate yields carbon oxysulphide, an offensive gas which burns with a blue flame; $KSCN + 2H_2SO_4 + H_2O = KHSO_4 + NH_4HSO_4 + COS$.

Potassium isothiocyanate, K·NCS, is said to be obtained by heating persulphocyanic acid with alcoholic solution of potash. The crystals are soluble in water; the solution does not give the red thiocyanate reaction with ferric salts. It is converted into normal thiocyanate by boiling or fusing. *Sodium thiocyanate* occurs in saliva.

Perthiocyanogen, or *pseudosulphocyanogen*, $C_3N_3S_3H$, is obtained as a yellow precipitate when potassium thiocyanate is heated with potassium chlorate and hydrochloric acid. It is used in dyeing (*canarin*).

Ammonium thiocyanate is prepared by acting on carbon bisulphide (7 parts by weight) dissolved in alcohol (30 parts) with strong ammonia (30 parts). After standing for a day or two, with occasional shaking, until all the CS_2 has dissolved, the red solution is distilled down to one-third of its bulk, when it becomes colourless, filtered if necessary, and allowed to crystallise;

$$CS_2 + 4NH_3 = CNS \cdot NH_4 + (NH_4)_2S.$$

It is also made on a large scale by boiling sulphur with the solution of ammonium cyanide from the gasworks. It crystallises like the potassium salt, and is very soluble in water, producing great cold. When heated, it fuses easily, and at 170° C., is metamerised into *thiocarbamide* (p. 671).

Lead thiocyanate, $Pb(CyS)_2$, forms a yellow crystalline precipitate.

Silver thiocyanate, AgCyS, is a white precipitate, very insoluble in water and in nitric acid, and sparingly soluble in ammonia.

Mercuric thiocyanate, $Hg(CyS)_2$, is a crystalline precipitate formed on stirring mercuric chloride with an alkali thiocyanate. It attracted much notice formerly as the toy called *Pharaoh's serpent*, which was a small cylinder of the thiocyanate mixed with gum, which burnt when kindled, evolving mercury and other vapours, and swelling to a bulky vermiform mass of mellone.

Cuprous thiocyanate, $Cu_2(CyS)_2$, precipitated by potassium thiocyanate from a cuprous salt, is very insoluble in water and in cold dilute acids, so that copper is sometimes precipitated in this form in quantitative analysis.

502. *Cyanogen sulphide*. Cy_2S, is obtained by decomposing cyanogen iodide, dissolved in ether, with silver thiocyanate; $CyI + AgCyS = Cy_2S + AgI$. It is a crystalline, fusible, volatile solid, soluble in alcohol and ether, but decomposed by water; potash converts it into cyanate and thiocyanate.

Phosphorus tricyanide, Cy_3P, is sublimed in tabular crystals from a mixture of silver cyanide and phosphorus trichloride, heated in a sealed tube at 140° C. for some hours, and distilled in a current of CO_2. It inflames at a very low temperature, and is decomposed by water into hydrocyanic and phosphorous acids; $Cy_3P + 3HOH = 3CyH + P(OH)_3$.

Cyanamide, $H_2N{\cdot}CN$, which also behaves as *carbodiimide*, NH : C : NH, may be obtained by fusing urea with sodium—$(NH_2)_2CO + Na = H_2N{\cdot}CN + NaOH + H$. The mass is dissolved in water, ammonia added in excess, and silver nitrate, which gives a yellow precipitate of $Ag_2N{\cdot}CN$; this is washed, dried, covered with ether, and decomposed by H_2S, when Ag_2S and $H_2N{\cdot}CN$ are produced, the latter dissolving in the ether, from which it may be crystallised.

Cyanamide may also be prepared, like other amides, by acting on NH_3, dissolved in ether, with gaseous CNCl; $NH_3 + CN{\cdot}Cl = H_2N{\cdot}CN + NH_4Cl$.

Another reaction which furnishes it is that between thiourea (p. 671) and mercuric oxide: $(NH_2)_2CS + HgO = H_2N{\cdot}CN + HgS + H_2O$. It forms crystals soluble in water, alcohol, and ether, and melting at 40° C. HCl passed into its ethereal solution gives crystals of $H_2N{\cdot}CN,2HCl$. Hydrolysis converts it into urea, and H_2S into thio-urea. With NH_3 it yields guanidine..

Dicyanimide, $HN(CN)_2$, is produced by the action of potash on solution of potassium cyanate: $3KOCN + H_2O = (KO)_2CO + KOH + HN(CN_2)$. On neutralising the solution with HNO_3 and adding $AgNO_3$, a precipitate of $AgN(CN)_2$ is obtained. Potassium isocyanate, K·NCO, does not yield dicyanimide.

The amides of cyanuric acid are (1) *melamine* or *cyanuramide*, $C_3N_3(NH_2)_3$, obtained by the action of NH_3 on cyanuric chloride, (2) *ammeline*, $C_3N_3(NH_2)_2OH$, produced by boiling melamine with HCl, and (3) *ammelide*, $C_3N_3NH_2(OH)_2$, formed by boiling melamine with KOH. Melamine crystallises from water, but the others are insoluble.

When NH_4SCN is heated, it loses NH_3 and H_2S, and is converted successively into *melam*, $C_6H_9N_{11}$, *melem*, $C_6H_6N_{10}$, and *mellone*, $C_6H_3N_9$, white amorphous compounds. *Potassium mellonide*, $C_9K_3N_{13}$, is formed when KSCN is heated out of contact with air, CS_2 being evolved; this crystallises with 3Aq and yields a corresponding silver salt and free acid.

Chrysean, $[CN{\cdot}CH(SH)]_2NH$, is obtained by covering potassium cyanide with water, in a flask, and saturating with H_2S gas;

$$4KCN + 5H_2S = C_4H_5S_2N_3 + 2K_2S + NH_4HS.$$

It crystallises from boiling water in golden needles, soluble in alcohol, ether, acids, and alkalies. Its alcoholic solution is red, and changes to a fugitive green on adding a little alkali.

503. *Alkyl cyanurates and isocyanates.*—The compounds recently described as alkyl cyanates are proved to be esters of imido-carbonic acid. By the action of CNCl on sodium alkyloxides, products are obtained which rapidly polymerise to alkyl cyanurates—*e.g.*, $3Cl{\cdot}CN + 3CH_3ONa = 3NaCl + (CH_3)_3O_3C_3N_3$.

Methyl isocyanate, or *methyl carbimide*, $H_3C{\cdot}NC{:}O$, was formerly regarded as the normal cyanate, being obtained by distilling potassium methyl sulphate with potassium cyanate; $KCH_3SO_4 + K{\cdot}O{\cdot}CN = H_3C{\cdot}NC{:}O + K_2SO_4$. It is also obtained by oxidising methyl isocyanide with mercuric oxide;

$$H_3C{\cdot}NC + HgO = H_3C{\cdot}NC{:}O + Hg.$$

It is a volatile liquid (b.-p. 44° C.) with a suffocating odour. When distilled

with potash, it yields methylamine, showing that the methyl is attached to the nitrogen, and that the compound is the isocyanate: $H_3C{\cdot}N:CO + 2KOH = H_3C{\cdot}NH_2 + CO(OK)_2$. Ammonia gas converts methyl isocyanate into *methyl urea* ($H_3C{\cdot}NC:O + NH_3 = NH_2{\cdot}NHCH_3{\cdot}CO$) resembling urea itself.

Dimethyl urea, $(NH{\cdot}CH_3)_2CO$, is formed by the action of water on methyl isocyanate; $2(H_3C{\cdot}NC:O) + H_2O = (NH{\cdot}CH_3)_2CO + CO_2$.

Ethyl isocyanate, or *ethyl carbimide*, $H_5C_2{\cdot}NC:O$, is prepared like the methyl compound, which it resembles. Its sp. gr. is 0·9 and it boils at 60° C. It yields ethylamine when distilled with potash, and triethylamine with sodium ethoxide; $H_5C_2{\cdot}NC:O + 2(C_2H_5{\cdot}ONa) = (H_5C_2)_3N + CO(ONa)_2$.

Ethyl urea, $NH_2{\cdot}NHC_2H_5{\cdot}CO$, *diethyl urea*, $(NHC_2H_5)_2CO$, and *triethyl urea* $(NHC_2H_5)N(C_2H_5)_2{\cdot}CO$, have been obtained.

Methyl-ethyl urea, $NHCH_3{\cdot}NHC_2H_5{\cdot}CO$, is formed by the action of methylamine on ethyl isocyanate; $H_5C_2{\cdot}NC:O + NH_2CH_3 = (NHCH_3)NHC_2H_5{\cdot}CO$.

504. The isothiocyanates of the hydrocarbon radicles are called *mustard oils* or *thiocarbimides*.

Allyl isothiocyanate, $H_5C_3{\cdot}NCS$, is the *essential oil of mustard*, obtained by grinding black mustard seeds with water and distilling. It does not exist in the seed, but is produced by the decomposition of *potassium myronate* contained in the seed, induced by a peculiar ferment called *myrosin*, which decomposes the myronate into the essence of mustard, glucose, and $KHSO_4$; $KC_{10}H_{18}NS_2O_{10} = H_5C_3{\cdot}NCS + C_6H_{12}O_6 + KHSO_4$. The seed yields about 0·5 per cent. of the oil.

The potassium myronate may be obtained from ground mustard by rendering the myrosin inactive by boiling alcohol, and then extracting the myronate with cold water. The solution is evaporated to a small bulk and mixed with alcohol, which precipitates the potassium myronate. The free acid is not known, being very unstable.

Myrosin is prepared by extracting ground white mustard with cold water, evaporating the filtrate to a syrup below 40° C., and adding alcohol in small quantity, when the myrosin is precipitated. It somewhat resembles albumin, being coagulated and rendered inactive by heat. Its aqueous solution, when added to potassium myronate, causes it in a few minutes to smell of mustard and become acid; it also becomes turbid from the separation of small globular cells like those of yeast. Myrosin occurs in other plants than mustard, such as the radish, rape, cabbage, and swede, all belonging to the same natural order as mustard (*Cruciferæ*). Mignonette root furnishes phenyl ethyl mustard oil, or phenyl ethyl isothiocyanate.

Essential oil of mustard has sp. gr. 1.017, and boils at 150° C. It is insoluble in water, but dissolves in alcohol and ether. It is the cause of the pungent odour of mustard paste and of its power to redden and irritate the skin. It is slowly decomposed by light, depositing a yellow precipitate. When heated with water at 100° C. for some time it loses sulphur and becomes *crotono-nitrile*, $C_3H_5{\cdot}CN$, which is present in considerable quantity in commercial mustard oil. When mustard oil dissolved in alcohol is acted on by HCl and Zn, it yields allylamine: $H_5C_3{\cdot}NCS + H_4 = H_5C_3{\cdot}NH_2 + HCHS$ (*thioformaldehyde*). By mixing mustard oil with ammonia and passing ammonia gas, *allyl-thio-urea*, or *thio-sinamine*, $NH_2{\cdot}NH(C_3H_5){\cdot}CS$, is obtained, forming prismatic crystals soluble in water, alcohol, and ether, and having a bitter taste. It is a weak base. When heated with lead hydroxide, it loses H_2S, and becomes *allyl-cyanamide*, $NHC_3H_5{\cdot}CN$, which afterwards polymerises into *sinamine*, or *tri-allyl melamine*, $(NHC_3H_5)_3(CN)_3$. This is a strongly alkaline base.

If allyl bromide be decomposed by ammonium thiocyanate, at a low temperature, *allyl thiocyanate*, $H_5C_3{\cdot}SCN$, is formed, which has no smell of mustard. When this is heated, it boils at 161° C., but the boiling-point soon falls, and a strong smell of mustard is perceived. When the boiling-point has reached

150° C., the whole distils over as allyl isothiocyanate, $H_5C_3{\cdot}NCS$, or mustard oil. Allyl thiocyanate, decomposed by potash, yields potassium thiocyanate and allyl alcohol; $H_5C_3{\cdot}SCN + KOH = H_5C_3{\cdot}OH + K{\cdot}SCN$; allyl isothiocyanate gives allylamine; $H_5C_3{\cdot}NCS + 4KOH = H_5C_3{\cdot}NH_2 + K_2S + CO(OK)_2 + H_2O$.

Mustard oil is also obtained artificially by distilling allyl iodide (p. 636) with potassium thiocyanate; $C_3H_5I + KSCN = C_3H_5{\cdot}NCS + KI$. When *ethyl* iodide is treated in the same way, ethyl thiocyanate, $C_2H_5{\cdot}SCN$ is obtained. To obtain the *ethyl isothiocyanate*, or *ethyl mustard oil*, or *ethyl thiocarbimide*, $C_2H_5{\cdot}NCS$, ethylamine dissolved in alcohol is digested with carbon bisulphide, distilled nearly to dryness, and the residue in the retort boiled with solution of $HgCl_2$. All primary amines yield the corresponding mustard oils when treated in this manner, and, since the odour is quite characteristic, the treatment with CS_2 and $HgCl_2$ is known as the *mustard-oil test for primary bases*.

The mustard-oil reaction is easily explained. When CO_2 is combined with dry NH_3, *ammonium carbamate* is formed; $CO_2 + 2NH_3 = CO(ONH_4)(NH_2)$. If CS_2 be substituted for CO_2 (the CS_2 employed in alcoholic solution), *ammonium thiocarbamate* is produced—$CS_2 + 2NH_3 = CS(SNH_4)(NH_2)$.

When ethylamine is used instead of ammonia, the product is *ethyl ammonium ethyl-thiocarbamate*; $CS_2 + 2NH_2(C_2H_5) = CS{\cdot}SNH_3(C_2H_5)NH(C_2H_5)$. On decomposing this with mercuric chloride, it yields the corresponding mercuric salt, which is decomposed, by boiling with water, into ethyl isothiocyanate, mercuric sulphide and hydrogen sulphide; $Hg(CS{\cdot}S{\cdot}NHC_2H_5)_2 = HgS + H_2S + 2C_2H_5NCS$.

Butyl isothiocyanate, $C_4H_9{\cdot}NCS$, is the *essential oil of scurvy-grass*, another cruciferous plant, and is sometimes sold as mustard oil, but it has a higher boiling-point, 160° C.

505. **Fulminates.**—The salts known as fulminates are prepared from the fulminates of mercury and silver, obtained when those metals are treated with nitric acid and alcohol. It is still doubtful what is their constitution, but the latest researches seem to show that they are salts of the acid C : N·OH, which may be regarded as the oxime (p. 625) of CO—*carboloxime*.

Mercuric fulminate $(C : N{\cdot}O)_2Hg$, is prepared on a small scale, with safety, by carefully observing the following directions:—Dissolve 1.6 grm. of mercury in 14 c.c. of ordinary concentrated nitric acid (sp. gr. 1.42) in a half-pint beaker, covered with a dial-glass; the dissolution may occur in the cold, or may be accelerated by gently heating. The solution contains $Hg(NO_3)_2$, HNO_3 and HNO_2. When all the mercury is dissolved, remove the beaker to a distance from any flame and pour into it, at arm's length, 17.5 c.c. of alcohol (sp. gr. 0.87). Very brisk action soon begins, and the fulminate separates as a crystalline precipitate; dense white fumes pour over the sides of the beaker, having the odours of nitrous ether and aldehyde; they also contain mercury compounds and HCN, and are very poisonous. When red fumes begin to appear abundantly, some water is poured in to stop the action (which occupies only two or three minutes), and the fulminate is collected on a filter, washed with water as long as the washings taste acid, and dried by exposure to air.

On a large scale the preparation is carried out under sheds. At Montreuil, 300 grams of mercury are dissolved in 3 kilos of colourless HNO_3, of sp. gr. 1.4 in the cold. The solution is transferred to a retort, and 2 litres of strong alcohol are added. In summer no heat is required, and the vapours are condensed in a receiver and added to a fresh charge. When the action has ceased, the contents of the retort are poured into a shallow pan, and, when cold, the fulminate is collected in a conical earthen vessel partially plugged at the narrow end. It is washed with rain-water, and drained until it contains 20 per cent. of water, being stored in that state.

Mercuric fulminate, thus prepared, has a grey colour from the presence of finely divided mercury, and sometimes contains mercuric oxalate. It may be purified by dissolving it in 100 parts of boiling water, which leaves the metal

and the oxalate undissolved, and deposits the fulminate on cooling in lustrous white prisms. It should not be kept in a stoppered bottle, as it would easily detonate by friction between the stopper and the neck of the bottle. The blow of a hammer causes it to detonate sharply with a bright flash and grey fumes of mercury; $HgC_2N_2O_2 = Hg + 2CO + N_2$. It is also detonated by being touched with a wire heated to 195° C., or by an electric spark, or by contact with strong sulphuric or nitric acid. Its sp. gr. being 4.4, a small volume of it evolves a large volume of gas; according to the above equation, the gas and vapour would occupy more than 1340 times the volume of the solid, at the ordinary temperature, and the volume at the moment of detonation would be much greater, because the fulminate evolves 403 units of heat (per unit) in its decomposition, and this would expand the evolved gases and greatly increase their mechanical effect. It is estimated that a pressure of 48,000 atmospheres is thus produced.

Fulminic acid, C : N·OH, is isomeric with cyanic acid, and was long supposed to contain the cyanogen group. It is doubtless obtained when fulminates are treated with HCl, when a smell of HCN is perceived although none is to be detected; but the fulminic acid immediately combines with the HCl, forming *chloroformoxime*, ClHC : N·OH, an indication that the carbon is unsaturated, as in CO. This oxime rapidly breaks up into formic acid and hydroxylamine hydrochloride; $ClHC:N\cdot OH + 2H_2O = NH_2OH.HCl + HCOOH$. Thus these two compounds and mercuric chloride are the products of the action of strong HCl on mercuric fulminate; by precipitating the mercury by H_2S and evaporating the solution, hydroxylamine hydrochloride may be crystallised, and this is one of the best methods for preparing this salt.

Mercuric fulminate is formed when $HgCl_2$ is added to *sodium nitromethane*, $CH_2 : NO\cdot ONa$, water being formed. This confirms the above constitution, but it must be added that the behaviour of the fulminate with halogens indicates the presence of a CN group. With Cl it yields $HgCl_2$, CNCl and CCl_3NO_2 (chlorpicrin), and with Br the reaction is similar, but *dibromonitro-aceto-nitrile*, $Br_2(NO_2)C\cdot CN$, is an intermediate product. Again, NH_3 converts the fulminate into urea and guanidine, as though it contained an isocyanic-group (see *Isocyanates*).

Cap composition.—The explosion of mercuric fulminate is so violent and rapid that it is necessary to moderate it for percussion-caps. For this purpose it is mixed with potassium nitrate or chlorate, the oxidising property of these salts possibly causing them to be preferred to any merely inactive substances, since they would tend to increase the temperature of the flash by burning the carbonic oxide into carbon dioxide, and would thus ensure the ignition of the cartridge. In the military caps, in this country, potassium chlorate is always mixed with the fulminate, and powdered glass is sometimes added to increase the sensibility of the mixture to explosion by percussion. Antimony sulphide is sometimes substituted for powdered glass, apparently for the purpose of lengthening the flash by taking advantage of the powerful oxidising action of potassium chlorate upon that compound (p. 186). Since the composition is very liable to explode under friction, it is made in small quantities at a time, and without contact with any hard substance. After a little of the composition has been introduced into the cap, it is made to adhere and waterproofed by a drop of solution of shell-lac in spirit of wine.

If a thin train of mercuric fulminate be laid upon a plate, and covered, except a little at one end, with gunpowder, it will be found, on touching the fulminate with a hot wire, that its explosion scatters the gunpowder, but does not inflame it. On repeating the experiment with a mixture of 10 grains of the fulminate and 15 grains of potassium chlorate, made upon paper with a card, the explosion will be found to inflame the gunpowder.

By sprinkling a thin layer of the fulminate upon a glass plate, and firing it with a hot wire, the separated mercury may be made to coat the glass, so as to give it all the appearance of a looking-glass.

Although the effect produced by the explosion of mercuric fulminate is very violent in its immediate neighbourhood, it is very slightly felt at a distance, and the sudden expansion of the gas will burst firearms, because it does not allow time for overcoming the inertia of the ball, though, if the barrel escape destruction, the projectile effect of the fulminate is found inferior to that of powder. It has been proved by experiment that the mean pressure exerted by the explosion of mercuric fulminate is very much lower than that produced by gun-cotton, and only three-fourths of that produced by nitroglycerine. Its great pressure is due

to its instantaneous decomposition into CO, N, and Hg vapour within a space not sensibly greater than the volume of the fulminate itself, which volume being very small, on account of the high density of the fulminate, the escaping gases exert an enormous pressure at the moment of explosion. This detonating property of mercuric fulminate renders it exceedingly useful for effecting the detonation of gun-cotton and nitroglycerine. Berthelot finds that even such stable gases as acetylene, cyanogen, and nitric oxide are decomposed into their elements by the detonation of mercuric fulminate. CS_2 is similarly decomposed (p. 239).

Silver fulminate, $(CN)_2(OAg)_2$ (?), is prepared in a similar way to the mercury salt. 0.65 gram of silver is dissolved, by gently heating, in 5 c.c. of ordinary strong HNO_3 (sp. gr. 1.42) and 3.5 c.c. of water. As soon as the silver is dissolved, the lamp is removed, and 14 c.c. of alcohol (sp. gr. 0.87) are added. If the action does not start shortly, a very gentle heat may be applied until effervescence begins, when the fulminate will be deposited in fine needles, and may be further treated like the mercuric salt. In some cases a little red HNO_3 is necessary to start the action. It may also be obtained as a crystalline precipitate by warming solution of $AgNO_3$ with HNO_3 and alcohol until effervescence begins.

Silver fulminate is far more dangerous than mercuric fulminate, and, if stored dry, should be wrapped up, in small portions, in paper. Even if wet, it is not safe, in a glass bottle. When dry, it should be lifted with a slip of card.

Silver fulminate crystallises in shining prisms, and is more soluble in boiling water (36 parts) than is mercuric fulminate; it detonates sharply when pressed with a hard body, or when heated a little above 100° C. When touched with a hot wire upon a piece of glass or thin metal, it gives a sharp report and shatters the plate, whilst mercuric fulminate emits a dull sound, and does not shatter unless closed in. Silver fulminate is used in toy crackers, such as the *pull crackers*, where it is mixed with powdered glass to increase the friction, and the *throw-down crackers*, where it is twisted up in thin paper with some fragments of quartz-pebble. It is occasionally mixed with mercuric fulminate in detonating tubes, to raise the note of the report.

Warm ammonia dissolves silver fulminate, and deposits, on cooling, crystals of *silver-ammonium fulminate*, $NH_4O{\cdot}CN{\cdot}O{\cdot}NCAg$, which is even more violently explosive, and is dangerous while still moist. A similar compound is formed with mercuric fulminate. Potassium chloride, added to a hot solution of silver fulminate, removes only half the silver as precipitated chloride, and the solution deposits shining plates of *silver-potassium fulminate*, $KO{\cdot}CN{\cdot}O{\cdot}NCAg$, which is very explosive. By the careful addition of HNO_3 the K may be exchanged for H, and the *silver hydrogen fulminate*, $HO{\cdot}CN{\cdot}O{\cdot}NCAg$, obtained, which dissolves easily in boiling water and crystallises on cooling; by boiling with silver oxide it is converted into silver fulminate, or, with mercuric oxide, into silver-mercury fulminate.

Zinc and *copper fulminates* may be obtained by decomposing moist mercuric fulminate with those metals; they are soluble, crystalline, and explosive.

Sodium fulminate is obtained by the action of sodium amalgam on an aqueous solution of mercuric fulminate. On evaporating over lime and sulphuric acid, the sodium salt is deposited in prisms (with $2H_2O$), which explode when rubbed. A crystalline compound of single molecules of sodium fulminate and mercuric fulminate, and 4Aq, has been obtained.

Fulminuric or *isocyanuric acid*, $HO{\cdot}NC(OC{\cdot}NH)_2$, is obtained as a potassium salt by boiling mercuric fulminate with potassium chloride. On adding silver nitrate, the sparingly soluble silver fulminurate crystallises out, and by decomposing this with H_2S, and evaporating the filtrate, a solution of the acid is obtained: it crystallises with difficulty, and is soluble in alcohol.

XI. PHENOLS.

506. The phenols are *hydroxy-benzenes*, *naphthalenes*, &c., derived from aromatic hydrocarbons by substituting hydroxyl for the nucleal hydrogen atoms, *e.g.*, *phenol*, $C_6H_5{\cdot}OH$; *orcinol*, $C_6H_3CH_3{\cdot}(OH)_2$; *pyrogallol*, $C_6H_3(OH)_3$; *naphthol*, $C_{10}H_7{\cdot}OH$. If the hydroxyl is introduced into the methyl group instead of the phenyl group in the homologues of benzene

(p. 548), an alcohol is produced; thus, $C_6H_5{\cdot}CH_2(OH)$ is *benzyl alcohol*, whereas $C_6H_4(OH){\cdot}CH_3$ is *methyl phenol* or *cresol*.

Phenols are distinguished from alcohols in combining more readily with alkalies, which caused them originally to be mistaken for acids. The phenolic hydroxyl is more acidic in character than the alcoholic hydroxyl, C_6H_5, &c., being more negative (acidic) than alcohol radicles; it is less acid, however, than the carboxylic hydroxyl contained in the true acids. Thus *sodium phenoxide*, $C_6H_5{\cdot}ONa$, is formed when phenol is dissolved in NaOH, but phenol does not dissolve in Na_2CO_3. Again, they do not yield aldehydes (or ketones) and acids when oxidised, being comparable in this respect with the tertiary alcohols; and when attacked by HNO_3 and H_2SO_4, they yield substitution-products, whereas the alcohols yield ethereal salts; thus, phenol yields *tri-nitrophenol* or *picric acid*, $C_6H_2(NO_2)_3{\cdot}OH$, and *phenol-sulphonic acid*, $C_6H_4(OH){\cdot}SO_2{\cdot}OH$. The phenols have a great tendency to produce coloured products of oxidation, and ferric salts generally colour them intensely.

The phenols are frequently products of the dry distillation of complex organic substances, *e.g.*, coal. They are also obtained by fusing the sulphonic acids with alkalies; thus benzenesulphonic acid yields phenol; $C_6H_5{\cdot}SO_2OK + KOH = C_6H_5{\cdot}OH + K_2SO_3$. The formation of phenols through the diazo-reaction has been already noticed (p. 681). Another general method sometimes employed is the distillation of aromatic hydroxy-acids either alone or with lime (see *Pyrogallol*).

The halogen-substituted benzenes are not attacked easily by alkalies, but when they contain nitro-groups they more readily exchange Cl for OH, forming nitrophenols; thus $C_6H_4(NO_2)Cl$ yields $C_6H_4(NO_2)OH$. The greater the number of nitro-groups the more readily this change occurs. The same remarks apply to the amido- and nitramido- benzenes.

Monohydric Phenols. (1) **Monohydroxybenzenes.—Phenol**, or *phenic acid*, or *carbolic acid* or *hydroxybenzene*, $C_6H_5{\cdot}OH$, is extracted from that portion of the heavy oil of coal-tar which boils between 150° C. and 200° C.

This is allowed to cool, when it deposits crystals of naphthalene, and is then well stirred with caustic soda of sp. gr. 1.34. On standing, two layers are formed, the upper consisting of the higher homologues of benzene, and the lower of an aqueous solution of sodium phenoxide. This is diluted with water, and exposed to air, when tarry oxidation-products separate, and the liquid is neutralised by successive additions of H_2SO_4, which first precipitates more tarry matters, then cresol and other homologues of phenol, and finally phenol itself as a light oil. It is purified by fractional distillation, the portion distilling between 180° C. and 190° C. being collected and artificially cooled, to crystallise the phenol.

Phenol is present in small quantity in urine, and in the trunk, leaves, and cones of the Scotch fir. It may be produced by the action of hydrogen peroxide on benzene; $C_6H_5{\cdot}H + HO{\cdot}OH = C_6H_5{\cdot}OH + HOH$. Benzene may also be directly oxidised to phenol by mixing it with aluminium chloride and passing oxygen gas. Benzenesulphonic acid, when distilled with fused potash, yields phenol—

$$C_6H_5{\cdot}SO_2{\cdot}OH + KOH = C_6H_5{\cdot}OH + KHSO_3.$$

Properties of phenol.—Phenol crystallises in needles, often several inches long, which smell strongly of coal-tar. It fuses at 43° C. and boils at 183° C. Fused phenol is slightly heavier than water (sp. gr. 1.084 at 0° C.). It dissolves in 15 parts of water at 20° C., and easily in alcohol and ether. It becomes pink or brown when kept, from the presence of some impurity. When two molecules of phenol (198 parts) are heated with one molecule (18 parts) of water, and cooled to

4° C., six-sided prisms of *phenol aquate*, $(C_6H_5\cdot OH)_2Aq$, are obtained, which fuse at 16° C. (61° F.). The commercial *carbolic acid crystals* generally consist of the aquate, and soon become liquid when the bottle is placed in warm water. It has a great tendency to remain superfused after cooling, solidifying suddenly on opening the bottle. The homologues of phenol, which accompany it in coal-tar, do not form crystalline aquates. Carbolic acid blisters the skin immediately; it is very poisonous, and arrests fermentation and putrefaction, so that it is largely used as an antiseptic. *MacDougall's disinfectant* is a mixture of phenol with calcium sulphite. *Calvert's disinfecting powder* consists of clay, with 12 or 15 per cent. of phenol.

When phenol vapour is passed through a red-hot tube, it yields benzene, toluene, xylene, naphthalene, anthracene, and phenanthrene. The aqueous solution of phenol gives a purple-blue colour with ferric chloride. With ammonia and chloride of lime, it gives a blue colour. With the mixture of mercuric nitrate and nitrous acid obtained by dissolving mercury in cold nitric acid, it gives a yellow precipitate, which dissolves with a dark-red colour in nitric acid.

Sulphuric acid (concentrated), to which 6 per cent. of potassium nitrite has been added, gives a brown colour, changing to green and blue, when gently heated with phenol. This is *Liebermann's* general *reaction for identifying phenols.*

Bromine water added to an aqueous solution of phenol produces a pale yellow precipitate of *tribromophenol*, $C_6H_2Br_3\cdot OH$, which redissolves until the bromine is in excess. This affords an excellent qualitative and quantitative test for phenol. If the precipitate be warmed with water and sodium amalgam, sodium phenoxide is produced, which gives the smell of phenol when heated with dilute sulphuric acid.

507. By passing phenol vapour over heated zinc-dust, it is converted into benzene: $C_6H_5\cdot OH + Zn = C_6H_6 + ZnO$. This is a *general method for the conversion of phenols into the corresponding hydrocarbons.*

Phenol forms a crystalline compound with CO_2, which is only stable under pressure, and may be obtained by heating salicylic acid in a sealed tube at 260° C.; $C_6H_4(OH)\cdot CO_2H = C_6H_5\cdot OH,CO_2$.

Potassium- and *sodium- phenol*, or *phenolates*, $C_6H_5\cdot OK$, $C_6H_5\cdot ONa$, are soluble crystalline bodies obtained by heating phenol with hydroxide or carbonate of the alkali (see p. 709).

508. Phenol is not attacked by acids, as alcohol is, yielding ethereal salts, but corresponding phenyl compounds are obtained by indirect processes. When phenyl is heated with PCl_5, it yields *chlorobenzene* and *phenyl orthophosphate:* the formation of chlorobenzene proves the existence of OH in phenol: $C_6H_5\cdot OH + PCl_5 = POCl_3 + C_6H_5\cdot Cl + HCl$. The phenyl orthophosphate results from the action of more phenol on the $POCl_3$: $POCl_3 + 3C_6H_5OH = PO(C_6H_5O)_3 + 3HCl$.

Phenyl hydrosulphide, or *thiophenol*, or *phenyl mercaptan*, $C_6H_5\cdot SH$, is formed by the action of phosphoric sulphide on phenol—

$$8C_6H_5OH + P_2S_5 = 2C_6H_5SH + 2(C_6H_5)_3PO_4 + 3H_2S.$$

It has an offensive odour, and boils at 169° C. Its extra-radicle hydrogen may be exchanged for metals, as usual with mercaptans. With mercuric oxide, it yields *mercuric thio-phenol*, $(C_6H_5S)_2Hg$. When mixed with ammonia and exposed to air, phenyl hydrosulphide is converted into *diphenyl disulphide*, a crystalline solid: $2C_6H_5SH + O = (C_6H_5)_2S_2 + H_2O$. *Diphenyl sulphide*, $(C_6H_5)_2S$, is obtained by distilling sodium benzene sulphonate with P_2S_5. It is an offensive liquid, boiling at about 292° C. Nitric acid converts it into *diphenylsulphone* or *sulphobenzide*, $(C_6H_5)_2SO_2$, which is also produced by the action of sulphuric anhydride on benzene: $2C_6H_6 + 2SO_3 = (C_6H_5)_2SO_2 + H_2SO_4$.

509. *Chlorophenols*, $C_6H_4Cl\cdot OH$, and the corresponding bromine and iodine substitution-products, are obtained by the action of those elements on phenol.

Nitrophenols, $C_6H_4(NO_2)OH$, *dinitrophenols*, $C_6H_3(NO_2)_2 \cdot OH$, and *trinitrophenol*, $C_6H_2(NO_2)_3 \cdot OH$, are produced when nitric acid acts on phenol. The last is known as *picric acid* (*v.i.*).

By reducing nitrophenols with tin and HCl, the NO_2 group is converted into the NH_2 group, and *amido-phenols* are produced. Dinitro- and trinitro-phenols admit of a partial conversion of the NO_2 groups, so that *amido-nitrophenols* are formed. The antipyretic *phenacetine* is a derivative of 1 : 4-amido-phenol and has the formula $C_6H_4(OC_2H_5)(NHCH_3CO)$, *p-acetamidophenetöl*.

510. **Picric** or *carbazotic acid*, or *trinitrophenol*, $C_6H_2(NO_2)_3 \cdot OH$, is best prepared by dissolving phenol (1 part) in strong sulphuric acid (1 part) and adding the solution of phenolsulphonic acids thus obtained to strong nitric acid (3 parts) by degrees. When the violent action is over the mixture is heated on the water-bath as long as much red gas is disengaged. On cooling, a crystalline mass of picric acid is obtained, which is purified by dissolving in boiling water, filtering, and crystallising. It is deposited in yellow plates or prisms, which are sparingly soluble in cold water, but more easily on heating, imparting a bright yellow colour to a large volume of water; alcohol dissolves it readily. Its solution has an intensely bitter taste (whence its name), and stains the skin and other organic matters yellow, which is turned to account in dyeing silk and wool. When heated, the crystals fuse at 122° C., with partial sublimation, and explode slightly at a higher temperature, in consequence of the sudden formation of gas and evolution of heat by the action of the NO_2 upon the C and H. This nitration of phenol into picric acid may be represented by the equation $-C_6H_5 \cdot OH + 3(HO \cdot NO_2) = C_6H_2(NO_2)_3OH + 3HOH$.

Picric acid is one of the very few acids which form sparingly soluble potassium salts; a cold saturated aqueous solution of picric acid is even a better test for potassium than is tartaric acid, giving, especially on stirring, a yellow adherent crystalline precipitate of *potassium picrate*, $C_6H_2(NO_2)_3OK$. This salt explodes violently when heated or struck, and has been used as an explosive. *Ammonium picrate* is also a very explosive salt. Picric acid precipitates several of the alkaloids. An alcoholic solution of picric acid forms crystalline compounds with several hydrocarbons in alcoholic solution, particularly with benzene, naphthalene, and anthracene. Reducing-agents, such as glucose, in alkaline solutions, convert picric acid into *picramic acid*, $C_6H_2(NO_2)_2(NH_2)OH$, which forms red salts. Gently heated with solution of chloride of lime, picric acid yields *chloropicrin*, or *nitrochloroform*, $C(NO_2)Cl_3$, recognised by its pungent tear-provoking odour.

Picric acid is a very common product of the action of nitric acid upon organic substances; indigo, silk, and many resins furnish it in considerable quantity, especially the fragrant red resin known as *Botany Bay gum*, obtained from one of the grass-trees of New South Wales, which is sometimes used for preparing picric acid. It is said that picric acid is used as a *hop-substitute* in beer; its presence would be shown by the fast yellow colour imparted to a thread of white wool soaked in the warm liquid.

The constitution of picric acid is expressed by the orientation $[OH : (NO_2)_3 = 1 : 2 : 4 : 6]$; this follows from the fact that it can be obtained by oxidising symmetrical trinitrobenzene with potassium ferricyanide, a change which results in the substitution of an OH for a hydrogen atom. A little consideration will show that this hydroxyl group can only take up a position between two nitro-groups if the trinitrobenzene is the symmetrical one (p. 547).

511. *Picramic acid*, or *2-amido-3-4-dinitrophenol*, $C_6H_2(NO_2)_2(NH_2)OH$, is prepared by reducing ammonium picrate in alcoholic solution by passing hydrogen sulphide, evaporating to dryness, and decomposing the ammonium picramate with acetic acid: $C_6H_2(NO_2)_3 \cdot ONH_4 + 3H_2S = C_6H_2(NO_2)_2(NH_2)ONH_4 + 2H_2O + S_3$. The picramic acid crystallises in red needles, which fuse at 165° C. It is soluble in water and alcohol, forming red solutions, which become blood-red on adding an alkali. The change of the yellow colour of potassium picrate to the dark red of potassium picramate by the action of a reducing-agent in the presence of excess of potash,

is employed in the examination of urine for the detection and estimation of glucose, which easily converts the picrate into picramate when heated. The picramates of potassium and ammonium form dark-red crystals.

512. *Phenol-sulphonic*, $C_6H_4(OH)SO_2OH$, and *disulphonic*, $C_6H_3(OH)(SO_2OH)_2$, *acids*, are obtained by dissolving phenol in strong sulphuric acid, $SO_2OH{\cdot}OH$. Orthophenolsulphonic acid rapidly changes by migration of the OH group, into the para-acid when warmed. The antiseptic *aseptol* is a solution of phenolsulphonic acid.

The sodium salt of *di-iodo-(para)phenolsulphonic acid*, $C_6H_2I_2OH{\cdot}SO_2OH$, has lately been introduced under the name of *sozoidol* as an antiseptic; it is said to be as effective as iodoform, and has no smell.

513. **Cresols**, or *methyl-phenols*, or *hydroxytoluenes*, $C_6H_4(CH_3)OH$, accompany phenol in coal-tar. The *coal-tar kreasote* is a mixture of phenol and cresol. The cresols may be prepared by dissolving the corresponding toluidines in sulphuric acid, adding potassium nitrate, and distilling by steam; $C_6H_4(CH_3)NH_2 + HNO_2 = C_6H_4(CH_3)OH + 2H_2O + N_2$.

Orthocresol is solid, fuses at 31° C., and boils at 188° C. *Metacresol* is liquid, and boils at 201° C. *Paracresol* is solid, fusing at 36° C., and boiling at 198° C.; they are metameric with benzyl alcohol, $C_6H_5{\cdot}CH_2{\cdot}OH$. Paracresol occurs in urine, and is a product of the putrefaction of albumin; its dinitro-derivative is a yellow dye, *Victoria orange*. Meta- and para-cresol give a blue colour with ferric chloride.

The presence of the OH group in the cresols protects the methyl group from the easy oxidation which characterises the methyl group of the toluenes. But the substitution of a radicle for the H of the OH group destroys the protective influence, and the methyl cresols $C_6H_4(CH_3){\cdot}OCH_3$ are easily oxidised to methoxybenzoic acids, $C_6H_4(COOH){\cdot}OCH_3$.

Creoline and *lysol* are sold as disinfectants; they are solutions of crude cresol in soap and water.

Methylisopropylphenols.—Thymol [$CH_3 : CH(CH_3)_2 : OH = 1 : 4 : 3$] occurs in oil of thyme. *Carracrol* [$CH_3 : CH(CH_3)_2 : OH = 1 : 4 : 2$] exists in the oil of *Origanum hirtum*, and is obtained by heating camphor with iodine.

514. (2) **Monohydroxynaphthalenes.—Naphthols**, $C_{10}H_7{\cdot}OH$, are prepared from naphthalenesulphonic acids or naphthylamines by the reactions described on pp. 681, 709. *α-Naphthol* melts at 94° C. and boils at 280° C.; *β-Naphthol* melts at 122° C. and boils at 286° C. The latter is the more soluble in water, and is used as an antiseptic.* The naphthols are true phenols, but they resemble the alcohols more nearly than the benzene phenols do. They give rise to a number of important dyestuffs, which are chiefly nitro-derivatives and diazo-derivatives. Thus, *dinitro-α-naphthol*, $C_{10}H_5(NO_2)_2{\cdot}OH$, is *Martius' yellow* or *naphthalene yellow*, and the sodium salt of its sulphonic acid is *naphthol yellow*, or *fast yellow*. The photographic developer *eikonogen* is *sodium amido-β-naphthol sulphonate*, $C_{10}H_5(OH)(NH_2)(SO_3Na)$.

Naphtholsulphonic acids are very numerous and a large number has been prepared both for settling the constitution of naphthalenes and for use as dyestuff components (p. 683), for which purpose the most important are the 1 : 4-monosulphonic acid, $C_{10}H_6(OH){\cdot}SO_3H$, (Neville and Winther's acid) and the 2 : 3 : 6- and 2 : 6 : 8-disulphonic acids, $C_{10}H_5(OH)(SO_3H)_2$, (R. and G. acids).

515. **Dihydric Phenols. Dihydroxybenzenes.—Pyrocatechol**, 1 : 2-$C_6H_4(OH)_2$, obtained by fusing potassium phenol-sulphonate with potash, $C_6H_4(OH)SO_2OK + KOH = C_6H_4(OH)_2 + K_2SO_3$, is found among the products of distillation of *catechu*, an astringent body extracted by boiling water from the inner bark wood of *Acacia catechu* and used in tanning. *Kino*, a similar extract from certain varieties of Pterocarpus, an Indian tree of the same botanical order, also furnishes it; as

* *Betol*, or *β-naphthyl salicylate*, $C_6H_4(OH){\cdot}COOC_{10}H_7$, is used in medicine like phenyl salicylate (salol).

do most vegetable extracts which contain tannin. The leaves of the Virginia creeper, a plant of the vine order, contains pyrocatechol. It is present in crude pyroligneous acid distilled from wood, and is said to be formed when cellulose, starch, or sugar is heated between 200° and 280° C. Pyrocatechol crystallises in prisms which fuse at 104° C. and boil at 245° C., though it begins to sublime below its fusing-point. It is very soluble in water, alcohol, and ether. It is a reducing-agent, precipitating Cu_2O from alkaline cupric solutions on warming, and reducing silver nitrate in the cold. In presence of alkalies it absorbs oxygen from the air, becoming brown. With ferric chloride, it gives a green colour, changed to red by alkalies. Nitric acid oxidises it to oxalic acid. It has weak acid properties, and was formerly called *oxyphenic acid.*

Guaiacol, or *methylpyrocatechol*, $C_6H_4(OH)OCH_3$, may be obtained by distilling *guaiacum*, a resinous exudation from the West Indian tree called *lignum vitæ*. The distillate is dissolved in ether, and mixed with alcoholic potash, which produces a crystalline mass of *potassium guaiacol*, which is washed with ether and decomposed by dilute sulphuric acid. It is also produced by heating to 180° C. a mixture of pyrocatechol, potassium methyl sulphate, and potash—

$$C_6H_4(OH)_2 + KCH_3SO_4 + KOH = C_6H_4(OH)OCH_3 + K_2SO_4 + HOH.$$

Beech-wood kreasote also contains it. Guaiacol forms colourless crystals, m.-p. 28° C. and b.-p. 203° C. It mixes sparingly with water, but easily with alcohol It gives an emerald-green colour with ferric chloride, and acts as a reducing-agent in alkaline solutions. When heated with hydriodic acid, it yields methyl iodide and pyrocatechol; $C_6H_4(OH)OCH_3 + HI = C_6H_4(OH)_2 + CH_3I$. It has the properties of a weak acid. When potassium guaiacol is heated with methyl iodide, it yields *veratrol* or *methyl guaiacol*; $C_6H_4{\cdot}OK{\cdot}OCH_3 + CH_3I = C_6H_4(OCH_3)_2 + KI$. Veratrol is an aromatic liquid, which may also be obtained by heating with baryta the *veratric* (*dimethyl-protocatechuic*) *acid*, extracted from sabadilla seeds;

$$C_6H_3(OCH_3)_2{\cdot}CO_2H + BaO = C_6H_4(OCH_3)_2 + BaCO_3.$$

Wood-tar kreasote contains phenol, cresol, *phlorol*, $C_6H_3(CH_3)_2{\cdot}OH$, guaiacol, and *creosol*, $C_6H_3(OCH_3)(CH_3)OH$. This last is obtained from that portion of the tar which distils at 221° C., by dissolving it in ether, and adding very strong KOH, which precipitates potassium-creosol, from which creosol is separated by H_2SO_4. It is an aromatic liquid, which yields *acetyl-creosol*, $C_6H_3(OCH_3)CH_3(OC_2H_3O)$, when treated with acetyl chloride, and this, when oxidised by permanganate, becomes *acetyl-vanillic acid*, $C_6H_3(OCH_3)CO_2H(OC_2H_3O)$, from which vanillic acid may be obtained by treatment with NaOH.

516. **Resorcinol**, 1 : 3-$C_6H_4(OH)_2$, was named from *resin*, being obtained from several bodies of that class, and *orcin*, with which it is homologous. It is now prepared on a large scale for the manufacture of colours by the action of caustic alkalies on benzene-disulphonic acid.

This acid is prepared by gradually adding benzene (4 parts) to fuming sulphuric acid, sp. gr. 2·244 (15 parts), gently heating for some hours, and finally at 275° C.; $C_6H_6 + 2H_2SO_4 = C_6H_4(SO_2{\cdot}OH)_2 + 2H_2O$. The 1 : 3-*benzene-disulphonic acid* forms a deliquescent crystalline mass on cooling. This is dissolved in a large quantity of water, neutralised with lime, and strained from the calcium sulphate formed by the excess of sulphuric acid. The solution of calcium benzene-disulphonate is decomposed by Na_2CO_3, the precipitated $CaCO_3$ filtered off, the solution evaporated to dryness, and the residue of sodium benzene-disulphonate fused with 2½ times its weight of caustic soda, at 270° C., for eight or nine hours; $C_6H_4(SO_2{\cdot}ONa)_2 + 2NaOH = C_6H_4(OH)_2 + 2SO_3Na_2$. The fused mass is dissolved in hot water, and boiled with HCl till all the SO_2 is expelled. The resorcinol is then extracted from the cooled aqueous solution by agitation with ether, and is obtained in crystals when the ether is distilled off.

Resorcinol is obtained in considerable quantity by distilling *extract of Brazil-wood*, a dye made by boiling the wood of *Cæsalpinia braziliensis* with water, and evaporating the solution. It was originally prepared by fusing with potash the

gum-resin known as *galbanum*, obtained in Turkey and the East Indies as an exudation from the *Galbanum officinale*, an umbelliferous plant. Other gum-resins obtained from plants of the same order also yield resorcinol when fused with potash; such as *ammoniacum*, *asafœtida*, *sagapenum*, all more or less fœtid-smelling medicinal bodies imported from the East. When these gum-resins are distilled alone, they yield *umbelliferone*, $C_9H_6O_3$, or $C_6H_4(CHO)_2CO$, which is converted into resorcinol when fused with potash.

Resorcinol crystallises in prisms or tables which fuse at 118° C., and boil at 276° C., but may be sublimed at a much lower temperature. It has a sweet taste, and is easily soluble in water, alcohol, and ether. Its solution gives a violet colour with ferric chloride. Exposed to air, it absorbs oxygen and becomes brown. Ammoniacal copper and silver solutions are reduced when heated with it. The most characteristic test for resorcinol consists in heating it with phthalic anhydride, (p. 617), dissolving in dilute sulphuric acid, and adding ammonia, when a splendid green fluorescence is produced, due to the formation of *resorcin-phthalein*, or *fluorescein* (*q.v.*).

The resorcinol of commerce sometimes contains *thioresorcinol*, $C_6H_4(SH)_2$, which may be obtained by reducing *benzenedisulphonic chloride*, $C_6H_4(SO_2Cl)_2$, with tin and hydrochloric acid; it melts at 179° C.

Styphnic acid, or *trinitroresorcin*, $C_6H(NO_2)_3(OH)_2$, so named from its astringent taste (στύφνος) is prepared from resorcinol just as picric acid is prepared from phenol, and by the action of nitric acid on those gum resins which yield resorcinol on fusion with potash. Styphnic acid forms yellow six-sided prisms or tables, sparingly soluble in cold water, but dissolving in alcohol and ether. It fuses at 175° C., and explodes when strongly heated, though it sublimes when heated gradually. It is a dibasic acid, and forms salts which are more explosive than the picrates. Ferrous sulphate and lime-water give a green colour with styphnic acid, and a blood-red with picric acid.

Dinitroso-resorcinol, $C_6H_2(NO)_2(OH)_2$, produced by the action of nitrous acid on a solution of resorcinol, is a dyestuff known as *fast green* or *solid green*.

Hydroquinone, or *quinol*, is the third (1 : 4) dihydroxybenzene; it will be considered under *quinone*.

517. **Orcin, or orcinol,** or 1 : 3 : 5-*dihydroxytoluene*, $C_6H_3CH_3(OH)_2$, is prepared from certain lichens, which are used by dyers for preparing the colours known as *litmus*, *cudbear*, and *archil*; such as *Lecanora tartarea*, or *rock-moss*, *Roccella tinctoria*, or *orchella weed*, and others. The lichens are boiled with lime and water for some time, the solution filtered, evaporated to one-fourth, treated with CO_2 to precipitate the lime, and shaken with ether to extract the orcin. Some orcin appears to exist ready formed in the lichens, but the greater part of it is formed by the action of the lime and water upon certain acids, which may be extracted from the lichens by lime in the cold, and obtained as gelatinous precipitates by adding HCl. Thus, *orsellinic acid*, $C_6H_2CH_3(OH)_2CO_2H$, when boiled with lime, yields carbon dioxide and orcin, $C_6H_3CH_3(OH)_2$.

Erythric acid, $C_{20}H_{22}O_{10}$, yields orcin and erythrite (p. 578); *evernic acid*, $C_{17}H_{16}O_7$, from the lichen *Evernia prunastri*, yields orcin and *everninic acid*, $C_9H_{10}O_4$.

Lecanoric acid, $C_{16}H_{14}O_7.H_2O$, when boiled with water, yields two molecules of orsellinic acid, $C_8H_8O_4$.

Orcin is also produced by the action of fused potash on aloes, the juice of a plant of the Liliaceous order (dragon's blood, obtained from the same order, yields phloroglucol). Orcin may be prepared from toluene, $C_6H_5{\cdot}CH_3$, by converting it into (ortho)chlorotoluenesulphonic acid, and fusing this with excess of potash—

$$C_6H_3Cl(CH_3){\cdot}SO_3H + 2KOH = KCl + KHSO_3 + C_6H_3CH_3(OH)_2.$$

Orcin crystallises in colourless six-sided prisms (with $1H_2O$), melting

at 58° C., or when anhydrous at 107°, and boils at 289° C. It tastes sweet and dissolves in water, alcohol, and ether; ferric chloride colours it violet.

It forms a crystalline compound with a molecule of ammonia, and when its solution in ammonia is exposed to air, it absorbs oxygen, becoming purple, and yielding with acetic acid a red colouring-matter, *orcéin*, $C_7H_8O_2 + NH_3 + O_3 = 2H_2O + C_7H_7NO_3$. This substance is the chief colouring-matter of the dyes prepared from lichens, by mixing them with lime and urine (to furnish ammonia), and exposing them to the air for some weeks. The colour is pressed out, and made into cakes with chalk or plaster of Paris.

Orcéin is sparingly soluble in water, but dissolves easily in alcohol and in alkaline liquids, yielding purple solutions which are reddened by acids, orcéin being precipitated.

518. **Trihydric Phenols. Trihydroxybenzenes.—Pyrogallin,** or *pyrogallol*, 1 : 2 : 3-$C_6H_3(OH)_3$, formerly called *pyrogallic acid*, is a phenol obtained by heating gallic acid—

$$C_6H_2(OH)_3{\cdot}CO_2H = C_6H_3(OH)_3 + CO_2.$$

To prepare it, gallic acid is heated with 2½ parts of water in a digester (*autoclave*) at 210°–220° C. for half an hour. The solution thus obtained is decolorised by animal charcoal and crystallised.

Pyrogallol may be sublimed from nut-galls heated to about 215° C., when the tannin is decomposed into pyrogallol and carbon dioxide: $C_{13}H_9O_7{\cdot}CO_2H + H_2O = 2C_6H_3(OH)_3 + 2CO_2$. It may be obtained synthetically by fusing *chlorophenol-sulphonic acid* (1 : 2 : 3) with potash—

$$C_6H_3Cl(OH)SO_3H + 2KOH = C_6H_3(OH)_3 + KCl + KHSO_3.$$

Pyrogallol crystallises in fine needles, which are felted together in light white tufts. It fuses at 132° C. and boils at 210° C. It is very soluble in water (2½ parts), alcohol, and ether. When its solution is mixed with an alkali, it at once absorbs oxygen from the air, becoming brown, and forming a carbonate, acetate, and other products, a little carbonic oxide being evolved. A mixture of potash and pyrogallin is employed to absorb oxygen in gas analysis. Pyrogallin is a strong reducing-agent, precipitating silver and mercury in the metallic state; its action on silver-salts renders it useful in photography and in hair-dyeing.

A pure ferrous salt gives no colour with pyrogallin, but a trace of ferric salt causes a blue coloration, while a pure ferric salt gives a red colour. When heated with phthalic anhydride, it yields *pyrogallol phthalein*, or *gallein*, $C_{20}H_{10}O_7$, which is used as a red dye. When chlorine is passed through a cooled solution of pyrogallol in acetic acid, *trichloro-pyrogallol*, $C_6Cl_3(OH)_3$, is obtained, and may be crystallised in needles, melting at 177° C.

Phloroglucol, 1 : 3 : 5-$C_6H_3(OH)_3$, was first obtained from a glucoside called *phlorizin*, existing in the bark of the apple-tree: the *glucol* refers to its sweet taste. It is also made, like resorcinol, by fusing certain vegetable extracts and gum-resins with caustic potash. It is thus obtained from *gamboge*, the resinous juice of *Garcinia gutta* (Ceylon), from *dragon's blood*, the resin of *Dracæna draco*, from *kino* (p. 712), *catechu*, and from the yellow dye-wood, *fustic*. The residue of the preparation of extract of fustic is fused with potash and a little water, dissolved in water, acidified with sulphuric acid, and shaken with ether, which extracts phloroglucol and protocatechuic acid: the ether is distilled off, and the aqueous solution of the residue mixed with lead acetate to precipitate the protocatechuic acid. The lead is precipitated by H_2S, and the phloroglucol again extracted by ether. It may also be prepared by fusing resorcinol (1 part) with soda (6 parts) until the mass has a light chocolate colour, when it is treated as above, omitting the separation of protocatechuic acid.

Phloroglucol is formed by fusing 1 : 3 : 5-*benzene-trisulphonic acid*, $C_6H_3(SO_2{\cdot}OH)_3$, with soda, or better by hydrolysing 1 : 3 : 5-triamido-benzene with HCl.

It crystallises in prisms with 2Aq, which it loses at 100° C. It fuses at 218°, and may be sublimed; it dissolves easily in water, alcohol, and ether, and reduces alkaline cupric solution. Ferric chloride gives a violet colour. Its solution in hydrochloric acid stains wood violet-red, and is an excellent test for woody tissue. Alkaline solutions of phloroglucol are oxidised by air, and become brown. When dissolved in ammonia, it yields a crystalline base; $C_6H_3(OH)_3 + NH_3 = H_2O + C_6H_3NH_2(OH)_2$ (*phloramine*). Other phenols do not so readily exchange OH for NH_2.

When phloroglucol is dissolved in acetic acid and treated with potassium nitrite, at a low temperature, it yields, on addition of excess of potash and alcohol, green needles of a very explosive body, which is the *potassium salt of tri-nitroso-phloroglucol*, $C_6O_3(NOK)_3$. When this is gradually added to a mixture of nitric and sulphuric acids, it is converted into *trinitro-phloroglucol*, $C_6(NO_2)_3(OH)_3$, which crystallises in yellow explosive prisms, and dyes wool and silk yellow like picric acid. It is a tribasic acid, and forms three series of coloured salts.

In most of its reactions, phloroglucol behaves as symmetrical tri-hydroxybenzene; but in the remainder it behaves as a triketone, yielding, for instance, a trioxime, $C_6H_6(N{\cdot}OH)_3$, with hydroxylamine (p. 625). From this it seems probable that phloroglucol exists in tautomeric forms (p. 701), namely,

$$CH{<}\begin{matrix}C(OH){\cdot}CH\\ C(OH){:}CH\end{matrix}{>}C(OH) \quad \text{and} \quad CH_2{<}\begin{matrix}CO{\cdot}CH_2\\ CO{\cdot}CH_2\end{matrix}{>}CO.$$

The first of these would represent a trihydroxybenzene (the enol form) containing a tertiary benzene ring, and the latter a triketone of hexamethylene, containing a secondary benzene ring.

1 : 2 : 4 -*Trihydroxybenzene* is called *hydroxyhydroquinone*.

518*a*. *Inosite*, $C_6H_{12}O_6 + 2H_2O$. This compound was formerly included among the sugars under the name of *flesh-sugar*, but inasmuch as (1) it does not behave as a reducing agent (see *Sugars*), (2) it yields a hexanitrate, $C_6H_6(ONO_2)_6$, when dissolved in strong HNO_3, and (3) it is converted into benzene and tetriodophenol when heated at 170° C. with HI, it is now known to be a cyclohexane derivative, probably *hexahydroxy-cyclohexane*, $C_6H_6(OH)_6$. It is obtained from the juice of beef: the chopped heart or lung of the ox is exhausted with water, the liquid pressed out, mixed with a little acetic acid, and heated to boiling. The liquid filtered from the coagulated albumin is mixed with lead acetate, filtered, and basic lead acetate added; this precipitates a lead compound of inosite, $2C_6H_{12}O_6.5PbO$, which is to be suspended in water and decomposed by H_2S, when the inosite passes into solution. The lead sulphide is filtered off, the solution evaporated on the water-bath, to a syrup, and mixed with ten volumes of alcohol and one of ether, when the inosite is precipitated. It forms prismatic crystals, which are sweet and soluble in 6 parts of water. It is but slightly soluble in weak alcohol, and insoluble in absolute alcohol and in ether. The crystals effloresce in air, and become anhydrous at 100° C. Inosite is optically active, occurring in the usual modifications. It undergoes lactic fermentation and is oxidised by nitric acid to oxalic acid. Inosite may be identified by moistening it with dilute nitric acid, evaporating almost to dryness, and adding ammoniacal calcium chloride, which produces a rose colour. Inosite solution mixed with a drop of mercuric nitrate gives a yellow precipitate, which becomes red when heated.

The proportion of inosite obtained from flesh is very small: many vegetables contain it more abundantly. The unripe French bean yields 0.75 per cent. of inosite; walnut-leaves in August, 0.3 per cent. It is also present in the leaves of ash and vine; grapes contain it, so that inosite is found in wine. Unripe peas, asparagus, and dandelions contain inosite. From these vegetables it may be extracted as from flesh. It has been found in urine in cases of Bright's disease.

Hexahydroxy-benzene, $C_6(OH)_6$, has been obtained by a circuitous process. It is crystalline, sparingly soluble in cold water, alcohol, and ether: the solutions absorb oxygen, becoming violet, and reduce silver nitrate. It is converted into benzene by distillation with zinc-dust.

Hexahydroxydiphenyl, $C_6H_2(OH)_3{\cdot}C_6H_2(OH)_3$, is the parent of the quinone *coeruligone*, $O : C_6H_2(OCH_3)_2{\cdot}C_6H_2(OCH_3)_2 : O$, which is obtained during the refining of crude acetic acid from wood by $K_2Cr_2O_7$: it is soluble in ordinary solvents, but crystallises from phenol in blue needles. It was formerly called *cedriret* in allusion to its interlaced crystals, (*cedria*, pitch; *rete*, a net). Tin and HCl convert it into

hydrocerulignone, $HO{\cdot}C_6H_2(OCH_3)_2{\cdot}C_6H_2(OCH_3)_2{\cdot}OH$, which is colourless, and yields hexahydroxydiphenyl when boiled with HCl. Hexahydroxydiphenyl dissolves in potash with a blue colour.

XII. QUINONES.

519. QUINONES are formed from aromatic hydrocarbons by the substitution of $(O_2)''$ for H_2, and are therefore products of oxidation.

Quinone, $C_6H_4(O_2)''$, or *benzoquinone*, may be obtained by heating benzene with chromyl chloride, when HCl is evolved and a brown solid compound produced; this is decomposed by water with formation of quinone, which remains dissolved in the excess of benzene—

(1) $C_6H_6 + 2CrO_2Cl_2 = 2HCl + C_6H_4(CrO_2Cl)_2$;
(2) $C_6H_4(CrO_2Cl)_2 + H_2O = C_6H_4(O_2)'' + Cr_2O_3 + 2HCl$.

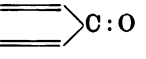
Many benzene derivatives also yield quinone when oxidised. It is best prepared by oxidising aniline with potassium dichromate and sulphuric acid.

One part of aniline is dissolved in a mixture of 8 parts of sulphuric acid with 30 parts of water, and 3½ parts of powdered potassium dichromate are slowly added to the cooled solution, which is then heated for some hours at about 35° C. After cooling, the liquid is shaken with ether, which extracts the quinone, and leaves it in golden yellow crystals when evaporated.

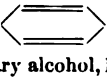
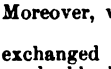
It is also obtained when quinic acid is oxidised with manganese dioxide and sulphuric acid; $C_6H_7(OH)_4CO_2H + O_2 = C_6H_4(O)_2'' + CO_2 + 4H_2O$. Many plant-extracts yield quinone when thus treated.

Quinone crystallises very easily in yellow prisms or plates, which sublime even in the cold, and fuse at 116° C., emitting a characteristic odour, and subliming in long golden needles in the presence of steam. It is sparingly soluble in cold water, but dissolves in hot water, and crystallises on cooling; alcohol and ether dissolve it. Its solution stains the skin brown. Quinone acts as an oxidising-agent, liberating iodine from hydriodic acid, and becoming converted into *hydroquinone*, or *quinol*, $C_6H_4(OH)_2$, which is 1 : 4 – dihydroxybenzene.

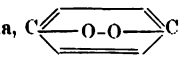
In many reactions quinone behaves like a diketone; for instance, with hydroxylamine it yields both a *monoxime*, $O : C_6H_4 : N{\cdot}OH$, and a *dioxime*, $HO{\cdot}N : C_6H_4 : N{\cdot}OH$ (*cf.* p. 625). The formula



has therefore been proposed (by *Fittig*) for quinone.

It has been pointed out, however, that if quinone contain true ketone groups, it should yield a secondary alcohol  when reduced, instead of, as is actually the case, the quasi-tertiary alcohol, hydroquinone,  .* Moreover, when substituted quinones react with PCl_5, each of the O atoms is exchanged for one Cl atom instead of two, as would be expected if the O were doubly linked to carbon. These considerations led

* Against this argument it may be urged that a ketone may give rise to a tertiary alcohol by reduction, as, for example, in the formation of pinacone from acetone (p. 575).

Graebe to the "peroxide" formula,  for quinone. Fittig's formula is, however, preferred.

That the oxygen atoms in quinone occupy the 1 : 4-position is shown by its easy conversion into 1 : 4-dihydroxybenzene, and by the fact that its dioxime yields 1 : 4-diamidobenzene when reduced.

Quinonemonoxime appears to be identical with the compound obtained by the action of nitrous acid on phenol, *nitroso-phenol*, $C_6H_4(OH)NO$, also obtained by treating *nitrosobenzene*, C_6H_5NO, with NaOH.

Hydroquinone is a constant product of the action of reducing-agents on quinone, and is best prepared by passing SO_2 through a warm saturated solution of quinone, when it is deposited in six-sided prisms, which fuse at 169° C., and sublime in monoclinic tables, so that hydroquinone is dimorphous. It is moderately soluble in water, and easily in alcohol and ether. Hydroquinone is distinguished from other dihydroxybenzenes (p. 712) by the action of oxidising-agents, such as Fe_2Cl_6, which converts it into fine green metallic prisms of *green hydroquinone*, or *quinhydrone*, $C_6H_4O_2{\cdot}C_6H_4(OH)_2$, also obtained by mixing aqueous solutions of quinone and hydroquinone. This is sparingly soluble in cold water, but dissolves in hot water to a brownish-red solution, which deposits the splendid green crystals on cooling. It dissolves in alcohol and ether with a yellow colour. It is readily dissociated into quinone and hydroquinone. Hydroquinone occurs among the products of distillation of the succinates, and has been produced from ethyl succinate by the following steps: Ethyl succinate, $C_2H_4(CO_2C_2H_5)_2$, acted on by sodium, yields *ethyl succinyl succinate*, $C_2H_4{\cdot}C_2H_2(CO)_2{\cdot}(CO_2{\cdot}C_2H_5)_2$; when this is treated with bromine, hydrogen is abstracted, leaving *ethyl quinol-dicarboxylate*, $C_6H_4O_2(CO_2{\cdot}C_2H_5)_2$. The acid obtained from this ethereal salt, *quinol-dicarboxylic acid*, $C_6H_4O_2(CO_2H)_2$, crystallises in needles, and yields a blue colour with ferric chloride. When distilled, it yields hydroquinone, $C_6H_4(OH)_2$, and $2CO_2$. As ethyl succinyl succinate may also be obtained by the action of sodium on ethyl bromacetoacetate, hydroquinone may be built up from acetic acid. It is used as a photographic developer.

Tetrachloroquinone, or *chloranil*, $C_6Cl_4(O_2)''$, is a frequent product of the action of chlorine or of a mixture of $KClO_3$ and HCl upon aromatic compounds, such as phenol, aniline, salicin, and isatin. It may be prepared from quinone by the action of $KClO_3$ and HCl, but more cheaply from phenol, by mixing it with potassium chlorate (4 parts) and adding it gradually to hydrochloric acid diluted with an equal volume of water. The mixture is gently heated, and more chlorate added, when a yellow mixture of *trichloroquinone*, $C_6HCl_3(O_2)''$, and tetrachloroquinone is precipitated. This is treated with sulphurous acid, which reduces the quinones to hydroquinones. The *tetrachlorohydroquinone*, $C_6Cl_4(OH)_2$, is insoluble in water, whilst the *trichlorohydroquinone*, $C_6HCl_3(OH)_2$, dissolves. The former is then oxidised by strong nitric acid, which converts it into chloranil. This body, which is used in colour-making, is yellow, insoluble in water, and sparingly soluble in alcohol; ether and benzene dissolve it, and deposit it in yellow crystals which may be sublimed. It is unattacked even by concentrated acids. Potash dissolves it with a purple colour, and yields purple crystals of potassium chloranilate: $C_6Cl_4O_2 + 4KOH = 2KCl + 2H_2O + C_6Cl_2(OK)_2O_2$. By dissolving the sparingly soluble potassium salt in hot water, and adding HCl, a red crystalline body is precipitated, which is *chloranilic acid*, $C_6Cl_2(OH)_2O_2.Aq$. It is soluble in water, with a violet colour, but sulphuric or hydrochloric acid precipitates it from the aqueous solution. *Bromanil*, $C_6Br_4(O_2)''$, has also been obtained from phenol.

Quinone chlorimides, $C_6H_4\begin{cases}O\\NCl\end{cases}$ and $C_6H_4\begin{cases}NCl\\NCl\end{cases}$, are obtained by the action of chloride of lime on 1 : 4-amidophenol and 1 : 4-diamidobenzene respectively.

By reaction of quinonechlorimide with phenols, *indophenols* are obtained; these are also formed by the oxidation of a mixture of phenol and a *p*-amidophenol. The typical indophenol is $O : C_6H_4 : N{\cdot}C_6H_4{\cdot}OH$.

Quinonechlorimide and a dialkylaniline react to form an *indoaniline*. These compounds are dyestuffs and are manufactured by oxidising a mixture of a paraphenylenediamine and a phenol. Thus *phenol blue*, $O : C_6H_4 : N{\cdot}C_6H_4{\cdot}N(CH_3)_2$,

is made by oxidising a mixture of *as*-dimethylparaphenylenediamine and phenol. By hydrolysis with H_2SO_4 it yields quinone and the original diamine.

By substituting an aniline for the phenol in the foregoing reaction, an *indamine* is produced. *Phenylene blue*, $NH : C_6H_4 : N{\cdot}C_6H_4{\cdot}NH_2$, is the compound obtained when a mixture of paraphenylenediamine and aniline is oxidised.

Naphthoquinones, $C_{10}H_6(O_2)''$.—*α-Naphthoquinone* [O : O = 1 : 4] is a true *paraquinone*, possessing the characteristic yellow colour, volatility and pungent odour of these quinones, and being reduced to naphthohydroquinone, $C_{10}H_6(OH)_2$. It is prepared by dissolving naphthalene (1 part), $C_{10}H_8$, in glacial acetic acid (6 parts) and oxidising with chromic anhydride (3 parts), dissolved in glacial acetic acid (2 parts). The mixture is boiled, and distilled after adding more water, when the naphthoquinone passes over with the steam. It is insoluble in water, sparingly soluble in cold alcohol, but dissolves in hot alcohol and in ether, crystallising in yellow tables, which fuse at 125° C., and sublime below 100°. Alkalies dissolve it, and it is oxidised by strong nitric acid into phthalic acid, $C_6H_4(CO_2H)_2$.

β-Naphthoquinone, [O : O = 1 : 2], is an example of an *ortho-quinone*, possessing the red colour, the non-volatility and the lack of odour characteristic of these. It is obtained by oxidising 1 : 2-derivatives of naphthalene.

520. **Anthraquinone**, $C_6H_4\begin{<}{CO}{CO}\end{>}C_6H_4$, is prepared by dissolving anthracene, $C_{14}H_{10}$, in glacial acetic acid, and adding chromic anhydride to the hot solution; on adding water, the anthraquinone is precipitated and may be purified by sublimation; it has no quinone odour. It sublimes in yellow needles, which are sparingly soluble in alcohol and ether, but dissolve in hot benzene and in nitric acid. It fuses at 285° C. and boils at 382° C. Potash does not dissolve it, but, when fused with KOH, it yields potassium benzoate. Sulphurous acid does not convert it into a hydroquinone, nor does hydriodic acid, but the latter reduces it to anthracene; as intermediate products of the reduction there are obtained the secondary alcohols, *hydroxyanthranol*, $C_6H_4\begin{<}{CO\text{——}}{CH(OH)}\end{>}C_6H_4$, and *anthranol*, $C_6H_4\begin{<}{CH(OH)}{CH(OH)}\end{>}C_6H_4$. Hence anthraquinone is more nearly a true diketone (*diphenylenediketone*) than is benzoquinone.

Anthraquinone may be synthetically prepared by heating phthalyl dichloride with benzene and zinc-dust;

$$C_6H_4\begin{<}{CO{\cdot}Cl}{CO{\cdot}Cl}\end{>} + C_6H_6 + Zn = C_6H_4\begin{<}{CO}{CO}\end{>}C_6H_4 + ZnCl_2 + H_2.$$

This synthesis shows that the CO groups must be attached to one of the benzene rings in the ortho-position to each other. That this is the case also with the other benzene ring is seen from the fact that when bromanthraquinone, $C_6H_3Br(CO)_2C_6H_4$ (synthesised, as above, from bromophthalyl chloride, $C_6H_3Br(COCl)_2$), is oxidised, the product is phthalic acid, not bromophthalic acid, showing that the brominated-ring has been removed, and that the CO groups must have been attached to the non-brominated-ring in the ortho-position.

Anthraquinone is chiefly important as the source of artificial alizarin.

521. **Alizarin**, or 1 : 2-*dihydroxyanthraquinone*,* $C_6H_4(CO)_2C_6H_2(OH)_2$, may be prepared from anthraquinone by treating it with bromine, which converts it into *dibromanthraquinone*, $C_6H_4(CO)_2C_6H_2Br_2$, and when this is heated to about 180° C. with potash, it yields *potassium alizarate*, $C_6H_4(CO)_2C_6H_2(OK)_2$; from the aqueous solution of this, hydrochloric acid precipitates alizarin.

* Anthracene derivatives are orientated similarly to those of naphthalene (p. 554).

Alizarin, one of the chief vegetable dyes, was formerly obtained exclusively from *madder*, the root of *Rubia tinctorum*, imported from the South of France and the Levant. It does not occur ready formed in the plant, but is produced by the decomposition of *ruberythric acid*, $C_{26}H_{28}O_{14}$, which may be extracted from madder root by cold water, and crystallises in yellow prisms. When the root is allowed to ferment, or is treated with H_2SO_4, the ruberythric acid is hydrolysed into alizarin and glucose, $C_{26}H_{28}O_{14} + 2H_2O = C_{14}H_8O_4 + 2C_6H_{12}O_6$. Alizarin is prepared on a large scale from anthraquinone by converting it into the sulphonic acid and fusing this with caustic soda.

The anthraquinone is made by treating anthracene, in leaden tanks, with potassium dichromate and diluted sulphuric acid, the reaction being completed by boiling. The anthraquinone is dissolved in strong sulphuric acid and re-precipitated by water, which retains the impurities in solution. After being washed and dried, it is heated for eight or ten hours at 160° C. with fuming sulphuric acid in an iron pot, being constantly stirred; on diluting with water, any unaltered anthraquinone is precipitated, and anthraquinone mono- and di-sulphonic acids, $C_6H_4(CO)_2C_6H_3(SO_3H)$, and $C_6H_3(SO_3H)(CO)_2C_6H_3(SO_3H)$, remain in solution.

The mixed sulphonic acids are neutralised with lime, and the calcium salts are decomposed by sodium carbonate. The concentrated solution of the sodium salts is heated with caustic soda and a little sodium chlorate, in a closed iron boiler, at about 180° C. for twenty-four hours, when a purple solution is obtained, containing the alizarate and anthrapurpurate of sodium. The sodium anthraquinone monosulphonate is first decomposed by the NaOH yielding sodoxyanthraquinone—

$$C_6H_4(CO)_2C_6H_3{\cdot}SO_3Na + 2NaOH = C_6H_4(CO)_2C_6H_3(ONa) + SO_3Na_2 + H_2O.$$

The sodoxyanthraquinone is then oxidised, by the oxygen from the chlorate, in presence of the excess of NaOH, into sodium alizarate—

$$C_6H_4(CO)_2C_6H_3(ONa) + O + NaOH = C_6H_4(CO)_2C_6H_2(ONa)_2 + H_2O.$$

The sodium anthraquinone disulphonate yields *sodium anthrapurpurate*—

$$C_6H_3(SO_3Na)(CO)_2C_6H_3(SO_3Na) + 7NaOH =$$
$$C_6H_3(ONa)(CO)_2C_6H_2(ONa)_2 + 2Na_2SO_3 + 4H_2O.$$

The solution is run into dilute sulphuric acid, when a mixture of alizarin and anthrapurpurin is obtained as a yellow precipitate.

Alizarin forms orange prisms (with $3H_2O$) very sparingly soluble in water, but easily soluble in alcohol and ether, and becomes red when dried. It fuses at about 290° C., and may be sublimed. It dissolves in strong H_2SO_4 with a deep-red colour, and is precipitated by water. It acts like a dibasic acid, dissolving in alkalies to purple solutions, which give purple-blue precipitates with salts of alkaline earths. The insolubility and the brilliant colours of the alizarates are of great value in dyeing and calico-printing. Alizarin gives red precipitates (*madder lakes*) with salts of Sn and Al, and a dark violet with salts of iron.

That alizarin is an adjacent dihydroxyanthraquinone follows from the fact that it can be synthesised from phthalic anhydride and 1 : 2-dihydroxybenzene (pyrocatechol) in the presence of sulphuric acid at 150° C. That the OH groups occupy the 1 : 2 (or 3 : 4 or 1′ : 2′ or 3′ : 4′, all these being the same in value as 1 : 2) position follows from the fact that alizarin yields two mono-substitution products in which the substituent is in the same ring as the OH groups; if the hydroxyl groups occupied the 2 : 3-positions this would not be possible, since the positions 1 and 4, which would then be vacant, are of the same value.

Anthrapurpurin, $C_6H_3{\cdot}OH{\cdot}(CO)_2{\cdot}C_6H_2(OH)_2$, is formed as above mentioned in the preparation of alizarin, and may be obtained by oxidising alizarin with MnO_2 and H_2SO_4. It resembles alizarin, but fuses at a higher temperature (330° C.) and is more soluble in water. The colours of its metallic salts are more brilliant than those given by alizarin, so that its presence in the artificial dye is advantageous.

Purpurin or 1 : 2 : 4-*tri-hydroxy-anthraquinone*, $C_6H_4(CO)_2C_6H(OH)_3$, is isomeric with the preceding, and is found accompanying alizarin in old madder root, and may be separated from it by boiling with alum, which dissolves only the purpurin. It may also be obtained by oxidising natural alizarin with MnO_2 and H_2SO_4.

Flavo-purpurin, $C_6H_3OH(CO)_2C_6H_2(OH)_2$, is sometimes formed in the manufacture of alizarin. It crystallises in golden needles soluble in alcohol.

Tetrahydroxy-anthraquinone, *anthrachrysone*, $C_6H_2(OH)_2(CO)_2C_6H_2(OH)_2$, or *alizarine-bordeaux*, is obtained by heating 1 : 3 : 5-dihydroxybenzoic acid, $C_6H_3(OH)_2{\cdot}COOH$, with H_2SO_4, which abstracts the elements of $2H_2O$ from two molecules of the acid.

Hexa-hydroxy-anthraquinone, $C_6H(OH)_3(CO)_2C_6H(OH)_3$, *rufigallic acid*, or *alizarine cyanine* (see p. 610), is prepared by heating gallic acid with H_2SO_4, which removes the elements of $2H_2O$ from two molecules of gallic acid, $C_6H_2(OH)_3{\cdot}COOH$. It is used as a red dye.

All these anthracene derivatives yield that hydrocarbon when heated with zinc-dust.

522. *Phenanthraquinone*, $\begin{matrix} C_6H_4{\cdot}CO \\ \vdots \\ C_6H_4{\cdot}CO \end{matrix}$, is prepared by oxidising phenanthrene (p. 554) with chromic acid. It crystallises in orange-yellow needles, melts at 198° C., and dissolves in hot alcohol. It is an ortho-quinone giving most of the reactions of a diketone.

Coerulignone (p. 716) is a derivative of the quinone of diphenyl.

Triphenylmethane Dyestuffs.

These compounds include the majority of the colouring-matters commonly called the aniline dyes.* Although they are amido- or hydroxyl derivatives, consideration of them has been postponed until now because they contain a benzene nucleus to which other groups are attached in a manner similar to that in which the oxygen atoms of quinone are linked to the benzene ring (*quinonoid structure*).

When three amido-groups or three hydroxyl-groups are introduced into triphenylmethane, $CH(C_6H_5)_3$ (p. 551), compounds are produced which are colourless, but readily become coloured when oxidised and treated with an acid. For example, triamido-triphenylmethane, $CH(C_6H_4NH_2)_3$, is a colourless substance; when oxidised it becomes triamidotriphenyl carbinol, $C(OH)(C_6H_4NH_2)_3$, which is also a colourless substance, and yields colourless salts (with one equivalent of acid) when treated with cold acids, but coloured salts when treated with warm acids. The latter salts are dyestuffs; they are formed from the carbinol by loss of a molecule of water, and since the only oxygen in the carbinol is that of the alcoholic group. OH, it must be supposed that this group forms water with the hydrogen of the acid. This loss of the OH group entails the conversion of the ordinary benzene linking of one of the benzene rings into the quinonoid linking, the change being accompanied by a development of colour, just as the conversion of the ordinary linking of hydroquinone (colourless) into the quinonoid linking of quinone, develops a colour. $HO{\cdot}C_6H_4{\cdot}OH$ becoming $O : C_6H_4 : O$. The following equation will make the change more clear :—

$$\underset{\text{Triamidotriphenylcarbinol hydrochloride (colourless).}}{HCl.\overset{v}{N}H_2{\cdot}C_6H_4{\cdot}C(OH)(C_6H_4{\cdot}NH_2)_2} = \underset{\text{Coloured salt † (Pararosaniline chloride).}}{Cl\overset{v}{N}H_2 : C_6H_4 : C(C_6H_4{\cdot}NH_2)_2} + H_2O.$$

The foregoing reactions are typical of the behaviour of every triphenylmethane

* It is here only possible to call attention to some typical "aniline dyes"; for information as to the chemical constitution of dyes of trivial names, the student must consult a work on dyestuffs.

† A simpler view of the constitution of this salt is that it is that of an ethereal chloride, derived from the carbinol by exchange of OH for Cl; $(C_6H_4{\cdot}NH_2)_3C{\cdot}Cl$. This view is not regarded as substantiated.

dyestuff; that is to say, each may be obtained by oxidising a derivative of triphenylmethane and treating the product with a warm acid. The parent triphenylmethane derivative is called the *leuco-base* of the dyestuff; the carbinol into which it is converted by oxidation is called the *colour-base* of the dyestuff; whilst the coloured salt is the dyestuff itself. Thus, triamidotriphenylmethane is called *leuco-pararosaniline*; triamidotriphenyl carbinol is *pararosaniline base*, whilst the coloured salt with the quinonoid linking is *pararosaniline chloride*. The converse changes are possible; that is to say, by treating the dyestuff with a caustic alkali the colour-base is precipitated, and if this be treated by reducing-agents (nascent hydrogen) it yields the leuco-base.

The triphenylmethane dyestuffs are classified into derivatives of:—(1) *Diamido-triphenylmethane*, $C_6H_5{\cdot}CH(C_6H_4{\cdot}NH_2)_2$; the type of these is *malachite green*. (2) *Triamidotriphenylmethane*, $CH(C_6H_4{\cdot}NH_2)_3$; the type of these is *rosaniline* (*magenta*). (3) *Trihydroxytriphenylmethane*, $CH(C_6H_4{\cdot}OH)_3$; the type of these is *aurin*. (4) *Triphenylmethane carboxylic acid*, $CH(C_6H_5)_2(C_6H_4{\cdot}CO_2H)$; the type of these is *eosin*.

Malachite green or *tetramethyl*-1 : 4-*diamido-triphenylmethane chloride*—

$$ClN(CH_3)_2 : C_6H_4 : C(C_6H_5)[C_6H_4{\cdot}N(CH_3)_2].$$

The leuco-base of this dyestuff is prepared by heating benzaldehyde with dimethylaniline and zinc chloride (to act as a dehydrating agent)—

$$C_6H_5{\cdot}CHO + 2C_6H_5{\cdot}N(CH_3)_2 = C_6H_5{\cdot}CH[C_6H_4{\cdot}N(CH_3)_2]_2 + H_2O.$$

The leuco-base is oxidised by PbO_2 (when it yields the corresponding carbinol or colour-base, see above) in the presence of HCl (to produce the colour-salt). The dyestuff is then precipitated by zinc chloride and sold in the form of a double zinc-salt.

Rosaniline salts constitute the bulk of the dyestuff known as *magenta* (*fuchsine*). They are formed by the action of acids on *rosaniline-base*, which is *triamidotolyldiphenyl carbinol*—

$$NH_2{\cdot}C_6H_3(CH_3){\cdot}C(OH)(C_6H_4{\cdot}NH_2)_2.$$

The *chloride*, $ClNH_2 : C_6H_3(CH_3) : C(C_6H_4{\cdot}NH_2)_2$, *nitrate* and *acetate* are the most common salts in the market. They are prepared by heating aniline oil for red (p. 665), which should contain equi-molecular proportions of aniline, orthotoluidine and paratoluidine, with an oxidising-agent (arsenic acid or nitrobenzene * is generally used);

$$NH_2{\cdot}C_6H_4{\cdot}CH_3 + \begin{matrix} C_6H_4(CH_3){\cdot}NH_2 \\ C_6H_5{\cdot}NH_2 \end{matrix} + O_2 = NH_2{\cdot}C_6H_4{\cdot}C(OH)\begin{matrix} C_6H_3(CH_3){\cdot}NH_2 \\ C_6H_4{\cdot}NH_2 \end{matrix} + 2H_2O.$$

The rosaniline base made in this way is converted into the chloride by adding hydrochloric acid, and this salt is precipitated by adding common salt. When recrystallised, rosaniline salts form bronze-green crystals which are sparingly soluble in cold water, but more readily in hot water, to a red solution. When the hot solution is mixed with ammonia and filtered quickly the rosaniline base crystallises from the filtrate in colourless plates which become red in air, from absorption of CO_2. Reducing-agents bleach the red solution with formation of *leucaniline*, $NH_2{\cdot}C_6H_3(CH_3){\cdot}CH(C_6H_4{\cdot}NH_2)_2$,† the leuco-base of rosaniline.

* This oxidising-agent is now more common than any other. When it is employed, HCl and iron filings form a part of the charge, so that the nitrobenzene is first reduced to aniline (which enters into the reaction), and the ferric chloride formed by its reduction is the immediate oxidant.

† When diazotised (p. 681), and heated with alcohol, leucaniline yields *metatolyldiphenylmethane*, $C_6H_4(CH_3){\cdot}CH(C_6H_5)_2$, (*cf.* p. 681), showing that leucaniline, and therefore rosaniline must be a derivative of this hydrocarbon.

Pararosaniline or *triamidotriphenol carbinol*, $C(OH)(C_6H_4\cdot NH_2)_3$, is prepared by oxidising a mixture of paratoluidine * (1 mol.) and aniline (2 mols.) in the same way as is described for rosaniline. The salts are red dyestuffs, like the rosaniline salts.

In both oxidations it may be supposed that the paratoluidine is oxidised to *p*-amidobenzaldehyde, which then condenses with the orthotoluidine and aniline (in the case of rosaniline) or with the aniline alone (in the case of pararosaniline).

Many derivatives of pararosaniline and rosaniline, containing methyl, ethyl and phenyl groups in place of the amido-hydrogen atoms, are prepared by heating pararosaniline or rosaniline chloride with alkyl or phenyl halides; these are also used as dyestuffs, the shade produced by them becoming more blue as successive alkyl or phenyl groups are introduced. Thus *pentamethyl-pararosaniline* is known as *methyl violet*, and *triphenyl-rosaniline chloride* as *aniline blue*. The combination of *tetramethylrosaniline*, which is saturated with methyl groups, with methyl chloride or iodide, produces a green dyestuff known as *iodine green*.

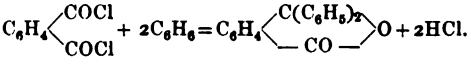
Aurin.—When pararosaniline base is diazotised (p. 681), the three NH_2 groups are converted into diazo-groups, and when the resulting compound is boiled with water it yields *trihydroxytriphenyl carbinol*, $(C_6H_4\cdot OH)_3C\cdot OH$, (*cf.* p. 681). This compound is very unstable and loses a molecule of water, becoming *aurin*, $O : C_6H_4 : C(C_6H_4OH)_2$, comparable in structure with pararosaniline chloride. It crystallises in green needles which dissolve in alkalies to a red solution, but are precipitated again by acids. Thus aurin behaves as an acid substance, as, indeed, is to be anticipated from the presence of phenolic OH groups. It will be noticed that, whilst pararosaniline is a type of *basic dyestuffs*, tending to combine with *acid mordants*, *aurin* is a type of *acid dyestuffs* tending to combine with *basic mordants*.

Rosolic acid bears the same relation to rosaniline as aurin bears to pararosaniline.

Eosin.—Triphenylmethane-carboxylic acid (see above), or rather its hydroxy-derivative *triphenyl carbinol-1:2-carboxylic acid*—

$$(C_6H_5)_2(C_6H_4\cdot COOH)C\cdot OH,$$

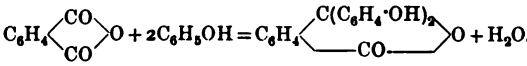
gives rise to the dyestuffs of this class. *Diphenylphthalide* is the lactam (p. 674) of this alcohol acid; it may also be regarded as derived from phthalic anhydride by substituting $(C_6H_5)_2''$ for O'', for it is prepared by the interaction of phthalyl chloride and benzene in presence of Al_2Cl_6—



Diphenylphthalide.

By substituting phthalic anhydride for the chloride, a phenol for the benzene and a dehydrating agent for the Al_2Cl_6 in this reaction, the eosin dyestuffs are obtained.

Thus, **phenol-phthalein** is obtained when phthalic anhydride is heated with two molecular proportions of phenol and $ZnCl_2$—



The mass is dissolved in an alkali and the phenophthalein precipitated by an acid. Its alkali salts are pink in solution, and are decomposed by the feeblest acids (see

* Its prefix appears to have been given to pararosaniline on account of the fact that paratoluidine is used in its manufacture. Since it has been recognised that paratoluidine is also necessary for rosaniline, the name has lost its significance.

p. 709), so that phenolphthalein is useful as an indicator in acidimetry. It can hardly be termed a dyestuff.

It has been supposed that phenolphthalein may behave as *dihydroxyphthalein*, $C_6H_4(COC_6H_4OH)_2$. As this does not import a quinonoid structure into its constitution, it has also been suggested that the salts of phenolphthalein are from the pseudoform $COOH{\cdot}C_6H_4{<}^{C_6H_4OH}_{C_6H_4:O}$. The ease with which the salts are decomposed by all acids seems to show, however, that they are derived from phenolic, not carboxylic groups.

Fluoresceïn, $C_6H_4{<}^{C[(C_6H_3{\cdot}OH)_2O]}_{\quad CO\quad}{>}O$, is formed when phthalic anhydride is heated with resorcinol, 2 mols. H_2O being liberated. It forms red crystals and dissolves in dilute alkalies, giving a solution which is red with a green fluorescence; this is also noticeable on the dyed fabric, hence the dyestuff is frequently mixed with others for producing a fluorescent green.

Eosin itself is a tetrabromo-derivative of fluoresceïn, and is made by brominating the latter in acetic solution. It dissolves in alkalies, giving a deep red solution which fluoresces green when diluted.

XIII. CARBOHYDRATES.

523. It has been already indicated (p. 584), that this group of organic compounds is only a temporary one in chemical classification, and that it will be broken up so soon as the true constitution of the compounds which it now comprises is understood. Indeed, it is already on the eve of extinction, since several of the sugars, formerly the typical members of the group, have been shown to be either aldehyde-alcohols or ketone-alcohols.

Originally, the compounds belonging to this class were such as contain hydrogen and oxygen in the proportion to form water, combined with six atoms, or some multiple of six atoms, of carbon. This is still true for a majority of the compounds of the class, but it is necessary now to describe several substances which do not fall in with the above definition, among the carbohydrates.

The carbohydrates may be divided into two groups: (1) the *Sugars*, and (2) the *Starches* and *Celluloses*.

The group of sugars contains compounds which are comparable in taste and other properties with the substance commonly called sugar. The molecular formulæ for the sugars may be said to be known in almost all cases, and it is found that whilst a number of them, such as glucose, $C_6H_{12}O_6$, correspond with the general formula, $C_n(H_2O)_n$, others, such as cane-sugar, $C_{12}H_{22}O_{11}$, correspond with the general formula, $C_n(H_2O)_{n-1}$. The molecular formulæ for the starches and celluloses are not known; but the percentage composition of these compounds indicates that their molecular formula is $(C_6H_{10}O_5)_n$. As may be expected, the compounds $C_n(H_2O)_{n-1}$ yield the compounds $C_n(H_2O)_n$ when decomposed by hydrolysis, and the compounds $(C_6H_{10}O_5)_n$ undergo a similar change.

The above considerations have given rise to a classification of the carbohydrates into (1) *saccharides* or *monoses*, $C_n(H_2O)_n$; (2) *disaccharides* or *saccharobioses*, $C_{12}H_{22}O_{11}$; (3) *trisaccharides* or *saccharotrioses*, $C_{18}H_{32}O_{16}$; (4) *polysaccharides*, $(C_6H_{10}O_5)_n$.

The Sugars.

524. These may be subdivided into *glucoses* (*aldoses* and *ketoses*), having the general formula $C_n(H_2O)_n$, *disaccharides* (formerly *sucroses*) or *saccharo-bioses*, having the formula $C_{12}H_{22}O_{11}$, and *trisaccharides*

or *saccharo-trioses*, having the formula $C_{18}H_{32}O_{16}$.* The sugars of the second and third classes are converted into sugars of the first class by hydrolysis. The type of the sugars of the first class is *grape-sugar*, that of the second *cane-sugar*, whilst that of the third is *raffinose*.

Since the sugars contain asymmetric carbon atoms, they give rise to a large number of optically active stereo-isomerides (p. 542).

525. **The Glucoses.**—These are named according to the number of carbon atoms which they contain—*e.g.*, *triose*, $C_3H_6O_3$; *tetroses*, $C_4H_8O_4$; *pentoses*, $C_5H_{10}O_5$; *hexoses*, $C_6H_{12}O_6$; *heptoses*, $C_7H_{14}O_7$, &c. In constitution they are either aldehyde-alcohols or *aldoses* (containing the group $\cdot CH(OH)\cdot CHO$), or ketone-alcohols or *ketoses* (containing the group $\cdot CO\cdot CH_2OH$), and accordingly behave as reducing-agents and yield hydrazones just as other compounds containing the aldehyde or the ketone group do.

The glucoses must be regarded as the first oxidation-products of polyhydric alcohols, the most important of which have been mentioned (p. 577). The aldoses would be formed by oxidation of the primary alcohol group, and the ketoses by oxidation of the secondary group. All the glucoses have asymmetric carbon atoms, and each exists in two stereoisomeric forms, the *d*- and the *l*- form, and in a third, externally compensated or racemic, inactive (*d* + *l*) form † (p. 605).

526. Thus the simplest aldose would be *glycollic aldehyde*, $CH_2OH\cdot CHO$, from glycol; glycerol yields both an aldose, glycerose (*aldotriose*), $CH_2OH\cdot CHOH\cdot CHO$ (p. 584) and a ketose, dihydroxyacetone (*ketotriose*), $CH_2OH\cdot CO\cdot CH_2OH$.

(1) **Tetroses.**—*Erythrose*, obtained by the oxidation of erythritol (p. 578) by the action of dilute nitric acid, is probably a mixture of the *aldotetrose*,

$$CH_2OH\cdot[CHOH]_2\cdot CHO,$$

and the *ketotetrose*, $CH_2OH\cdot CHOH\cdot CO\cdot CH_2OH$. A *d*- and an *l*- form are known.

(2) **Pentoses.**—The *aldopentoses*, $CH_2OH\cdot[CHOH]_3\cdot CH_2OH$ are alone known at present. They are natural sugars, occurring in many plants. They resemble the aldohexoses (*r.i.*) in their general behaviour except that they are not fermented by yeast. Other characteristics are that they yield furfural (p. 586) or its homologues when distilled with dilute acids, and that they give a red colour with phloroglucinol and HCl.

Eight optically active and four externally compensated aldopentoses are possible (p. 621). *l-Arabinose*, the chief member of the class, is prepared by boiling with dilute H_2SO_4 gum arabic and other gums which yield little mucic acid when oxidised by HNO_3. It crystallises in sweet prisms, melts at 160° C. and is strongly dextro-rotatory.†

By reduction it yields the pentatomic alcohol *arabitol*, $CH_2OH\cdot[CHOH]_3\cdot CH_2OH$. *Xylose* (from wood-gum, straw, and jute), and *ribose* are isomerides of arabinose. *Rhamnose* (from quercitrin) and *fucose* (from sea-weed) are methyl arabinose, $C_5H_9(CH_3)O_5$.

(3) **Hexoses, $C_6H_{12}O_6$.**—These are the compounds which were originally called *glucoses*. They are widely distributed in nature, but are mainly found in unripe fruit, the chief being dextrose, or grape-sugar, and lævulose, or fruit-sugar; they are produced by the hydrolysis of the disaccharides and polysaccharides, the change being effected both by enzymes and by dilute acids or alkalies. *d*-Glucose, *d*-mannose,

* According to one system of nomenclature the termination *-ose* is employed to designate sugars of the first class, and the termination *-on* to indicate sugars of the second class. Thus $C_6H_{12}O_6$ is *hexose*, whilst $C_{12}H_{22}O_{11}$ is *dihexon*.

† Much confusion is engendered by Fischer's custom of naming the sugars *d*- and *l*- without reference to their actual rotation, but according to the way in which they are derivable from each other.

d-galactose, and *d*-fructose are fermented by yeast, yielding alcohol. A few have been synthesised, and the constitution of nearly all has been settled (see below).

(*a*) *Aldohexoses*, $CH_2OH{\cdot}[CHOH]_4{\cdot}CHO$.—The substance commonly called **glucose, grape-sugar** or **dextrose** is *d*-glucose, there being also an *l*-glucose and a (*d* + *l*)-glucose. It is the aldehyde of sorbitol (p. 579).

d-Glucose is the crystallised sugar found in honey, raisins, and many other fruits; it is almost always accompanied by lævulose, a keto-hexose, which is far more difficult to crystallise. Dextrose is also found in small quantity in several animal fluids, and in the liver, and it is abundant in urine in cases of *diabetes*.

Dextrose may be obtained from honey by mixing it with cold alcohol to dissolve the lævulose, which forms about one-third of its weight, and leaves about an equal quantity of dextrose, which may be dissolved in boiling alcohol and crystallised. To extract it from fruits, they are crushed with water, strained, the liquid boiled to coagulate albumin, filtered, evaporated to a syrup, and set aside for some days, when crystals of dextrose are deposited. Fresh fruits contain chiefly lævulose, which is gradually converted into dextrose.

Dextrose is also a product of the hydrolysis of glucosides (*q.v.*), and di- and poly-saccharides (cane-sugar, starch, &c.).

From cane-sugar it is best prepared by heating a mixture of 250 c.c. of alcohol (sp. gr. 0.823) with 10 c.c. of strong HCl to 45° C. and adding 80 grams of finely powdered cane-sugar in small doses. When the sugar has entirely dissolved, the whole is set aside for a week and stirred to induce crystallisation. The crystals of dextrose are drained from the solution containing lævulose and washed with alcohol.

Commercial glucose or *starch-sugar* is made by heating starch with diluted sulphuric acid,* which first converts it into dextrin and finally into *d*-glucose, $(C_6H_{10}O_5)_n + nH_2O = nC_6H_{12}O_6$.

Water containing about 1.5 per cent. of H_2SO_4 is heated to boiling and a hot mixture of starch and water is allowed to flow gradually into it. The mixture is boiled for half an hour, neutralised with chalk, and concentrated by evaporation, when it deposits crystals of calcium sulphate. The clear syrup is drawn off and evaporated in a vacuum-pan till it is strong enough to crystallise, some glucose from a previous batch being added to promote crystallisation. The glucose thus obtained contains about 70 per cent. of *d*-glucose and also maltose, dextrin, and some calcium salts of organic acids; it may be purified by washing with strong alcohol mixed with 3 per cent. of HCl, and afterwards with commercial absolute alcohol.

When crystallised from an aqueous solution, dextrose forms six-sided scales (with $1H_2O$); these fuse at 86° C., and become anhydrous at 110° C.; it crystallises from alcohol at 30° C. in small anhydrous needles, which melt at 146° C. It is less sweet than cane-sugar, and can be directly fermented by yeast (p. 561). Glucose dissolves in 1.2 parts of cold water, in 50 parts of cold, and in 5 parts of boiling, alcohol (sp. gr. 0.837). When heated to 170° C., it is converted into *dextrosan* (*glucosan*), $C_6H_{10}O_5$, a nearly tasteless substance, convertible into glucose by dilute acids. When boiled with caustic potash, glucose gives a dark brown solution, being ultimately converted into humus-like acids. In presence of alkalies, glucose acts as a strong reducing-agent. If a solution of glucose be mixed with $CuSO_4$, and KOH be gradually added, the blue precipitate of cupric hydroxide produced at

* Care should be taken that the sulphuric acid is free from arsenic, lest the latter pass into the glucose and thence into the beer brewed therefrom.

first dissolves in excess of potash to a fine blue solution; if this be gently heated, a yellow precipitate of cuprous hydroxide is produced, which becomes red cuprous oxide when boiled; a little metallic copper is precipitated at the same time, and the glucose is oxidised to a number of organic acids. Glucose precipitates metallic silver when warmed with ammonia-nitrate of silver, and metallic mercury from $Hg(CN)_2$ mixed with KOH.

Solution of glucose mixed with NaCl deposits crystals of $2C_6H_{12}O_6.NaCl.H_2O$, which is sometimes deposited from diabetic urine. Glucose is not so easily blackened by H_2SO_4 as is sucrose, but forms an unstable compound with it. With alkaline earths dextrose combines to form compounds like $C_6H_{12}O_6.CaO$, which are precipitated by alcohol. Other reactions will be discussed under *Constitution of the Sugars*.

Dextrose rotates the plane of polarisation to the right hand, but a solution which has been kept for some hours has only half the effect of a freshly made solution, a phenomenon known as *bi-rotation*, and probably due to the formation of hydrates.

Glucose is used by brewers and distillers for making alcohol, and by confectioners; dyers and calico-printers use it to reduce indigo.

d-Mannose is obtained, together with lævulose, by the cautious oxidation of mannitol (p. 578), with platinum black or nitric acid. It may be prepared by boiling *seminine*, the reserve-cellulose of many seeds, with dilute H_2SO_4; it is sometimes called *seminose*. Mannose has not been crystallised; it is very soluble in water, and its solution is dextro-rotatory; a *l* and a (*d* + *l*)- form are also known.

d-Galactose is obtained, together with *d*-glucose, when milk-sugar and some varieties of gum arabic are boiled with dilute H_2SO_4. To prepare it, milk-sugar is boiled for six hours with four parts of water containing 5 per cent. of H_2SO_4. The solution is precipitated by baryta, filtered, evaporated to a syrup, and induced to crystallise by adding a few crystals of dextrose. The crystals are washed with alcohol of 80 per cent., and recrystallised from hot alcohol of 70 per cent. It crystallises in rhombic prisms, which are less sweet than cane-sugar, and melts at 166° C. It is not very soluble in cold water, and is insoluble in absolute alcohol. Galactose is also obtained by hydrolysing *galactitol*, $C_9H_{18}O_7$, a crystalline substance extracted by alcohol from yellow lupines. *l*- and (*d* + *l*)-galactose are known.

The *guloses* and *taloses* are artificial aldohexoses. *Methylhexose* or *rhamnohexose*, $C_6H_{11}(CH_3)O_6$, has also been prepared.

(*b*) *Ketohexoses*, $CH_2OH{\cdot}[CHOH]_3{\cdot}CO{\cdot}CH_2OH$.—*d*-**Fructose** is the most important of these. It is commonly known as **fruit-sugar** or **lævulose**, and is prepared by heating cane-sugar with water and a very little sulphuric acid on a water-bath for half an hour, removing the acid by barium carbonate, and evaporating to a syrup. This syrup contains *invert-sugar*, a mixture of equal weights of dextrose and lævulose, which mixture deposits crystals of dextrose when exposed to light. To obtain pure lævulose, it is mixed with water, cooled in ice, and stirred with calcium hydroxide, which precipitates a sparingly soluble lime compound of lævulose. This is suspended in water and decomposed by CO_2; the filtrate from the calcium carbonate is then evaporated on a water-bath. The syrup is washed with cold alcohol and set aside in a cold place, when the lævulose crystallises.

Lævulose is much sweeter than dextrose, rivalling cane-sugar in this respect. It does not ferment so readily as dextrose, so that when invert-sugar is mixed with yeast, the dextrose is the first to disappear. It also reduces alkaline cupric solutions (p. 619) less readily. Lævulose rotates the plane of polarisation of light to the left, whence its name, but a

dextro- (*l*) and an inactive (*d* + *l*) lævulose also exist. It forms two crpstalline compounds with lime, $C_6H_{12}O_6.CaO.2Aq$ and $C_6H_{12}O_6.3CaO$, dissolving respectively in 137 and 333 parts of cold water.

When heated to 170° C., lævulose is converted into *lævulosan*, $C_6H_{10}O_5$, which is dextro-rotatory. When heated with alkalies it is partly converted into *d*-glucose and *d*-mannose.

527. (4) **Heptoses**, $C_7H_{14}O_7$, **octoses**, $C_8H_{16}O_8$, and **nonoses**, $C_9H_{18}O_9$.—It has been found possible to produce a glucose containing x carbon atoms from one containing x-1 carbon atoms by treating the latter with hydrocyanic acid, whereby it is converted into a cyanohydrin (p. 582) just as any other aldehyde or ketone would be. This cyanohydrin is convertible into a carboxylic acid by hydrolysis; this may be reduced to a new sugar by sodium amalgam; thus, dextrose yields the cyanohydrin $CH_2OH{\cdot}[CHOH]_4{\cdot}CH(OH){\cdot}CN$, which is converted into *dextrose-carboxylic acid* (*gluco-heptonic acid*), $CH_2OH{\cdot}[CHOH]_5{\cdot}CO_2H$, by hydrolysis, and when this acid is reduced it yields *glucoheptose*, $CH_2OH{\cdot}[CHOH]_5{\cdot}CHO$. By these means each glucose may be made to yield a heptose, which, in its turn, may be converted into an octose and a nonose; consequently the possible number of these sugars is very large. They have not been found in nature.

528. **Synthesis of the Glucoses.**—The key to the synthetical production of the glucoses was phenylhydrazine. Like other aldehydes and ketones the glucoses form hydrazones when heated with a solution of phenylhydrazine hydrochloride and sodium acetate (p. 685). Thus the aldohexoses form the hydrazones

$$CH_2OH{\cdot}[CHOH]_3{\cdot}CHOH{\cdot}CH : N{\cdot}NC_6H_5,$$

while the hydrazones from the ketohexoses have the form

$$CH_2OH{\cdot}[CHOH]_3{\cdot}C(: N{\cdot}NHC_6H_5){\cdot}CH_2OH.$$

When an excess of phenylhydrazine is used, the hydrazones lose H_2 on account of the tendency for $C_6H_5NH{\cdot}NH_2$ to absorb H_2 and become $C_6H_5NH_2$ and NH_3 (p. 685). This converts the aldose hydrazone into a ketonic compound and the ketose hydrazone into an aldehydic compound—

$$CH_2OH{\cdot}[CHOH]_3{\cdot}CO{\cdot}CH : N{\cdot}NHC_6H_5$$
$$CH_2OH{\cdot}[CHOH]_3{\cdot}C(: N{\cdot}NHC_6H_5){\cdot}CHO.$$

These immediately combine with a second molecule of phenylhydrazine to form *osazones*, both of which have the formula,

$$CH_2OH{\cdot}[CHOH]_3{\cdot}C(: N{\cdot}NHC_6H_5){\cdot}CH : N{\cdot}NHC_6H_5.$$

Thus the aldoses and ketoses yield the same osazones except in so far as these may differ stereochemically.

The hydrazones are generally soluble in water, but the osazones are bright yellow, sparingly soluble, and easily crystallised. Thus their formation is often the best method of identifying a known sugar or of isolating a new one.

For this latter purpose the osazone is dissolved in cold strong HCl; it is thus converted into the corresponding *osone*, a ketone-aldehyde;

$$CH_2OH{\cdot}[CHOH]_3{\cdot}C(: N{\cdot}NHC_6H_5){\cdot}CH : N{\cdot}NHC_6H_5 + 2HCl + 2H_2O$$
$$= CH_2OH{\cdot}[CHOH]_3{\cdot}CO{\cdot}CHO(\textit{glucosone}) + 2C_6H_5NH{\cdot}NH_2HCl.$$

The red liquid which is formed deposits phenylhydrazine hydrochloride; it is filtered and neutralised with $PbCO_3$; the lead compound of the osone remains in solution; it is precipitated by baryta and the precipitate decomposed by H_2SO_4. To convert the solution of the osone, thus obtained, into a sugar it is reduced by means of zinc and acetic acid;

$$CH_2OH{\cdot}[CHOH]_3{\cdot}CO{\cdot}CHO + H_2 = CH_2OH{\cdot}[CHOH]_3{\cdot}CO{\cdot}CH_2OH.$$

When dextrose is treated in this way it is converted into lævulose.

529. Formaldehyde is the first step in synthesising glucoses from their elements. Treated with lime-water, it is polymerised to a mixture of sugars, termed *formose;* a similar mixture (methylenitan) is obtained from trioxymethylene (p. 581) in like manner. Two sugars, α- and β-*acrose*, have been isolated from this mixture and also from the mass obtained by treating glycerose (p. 584) with alkalies. They are separated by taking advantage of the greater solubility of β-acrosazone, than of α-acrosazone, in ethyl acetate.

The glucose recovered from α-acrosazone in the manner described above appears to be identical with (*d*- + *l*)-fructose, which by fermentation with yeast is converted

into *l*-fructose, the *d*-constituent having been used by the yeast (see p. 606). This *l*-fructose is dextro-rotatory (see foot-note, p. 725), and is not the lævulose found in nature. When (*d* + *l*)-lævulose (from a-acrose) is reduced by sodium amalgam, it yields (*d* + *l*)-mannitol, $CH_2OH{\cdot}[CHOH]_4{\cdot}CH_2OH$, which may be oxidised to (*d* + *l*)-*mannonic acid*, $CH_2OH{\cdot}[CHOH]_4{\cdot}CO_2H$. This can be resolved by crystallisation of its strychnine salt into *l*- and *d*-mannonic acids, which by reduction yield first *l*- and *d*-mannose and then *l*- and *d*-mannitol. By taking *l*- and *d*-mannose through the phenylhydrazine reactions they yield *l*- and *d*-fructose.

When *l*- and *d*- mannonic acids are heated with quinoline they are converted into *l*- and *d*- *gluconic acids*, which are stereo-isomeric with them. By reduction, the gluconic acids yield *l*- and *d*-glucose (dextrose). Thus a number of hexoses has been synthesised.

It will be observed that the monocarboxylic acids derived from the polyhydric alcohols are useful transition products in the syntheses, as they readily lend themselves to resolution by means of their salts with the alkaloids.

Through these acids also it is possible to pass from the pentoses to the hexoses and *vice versâ*. Thus *l*-arabinose combines with HCN as any other aldehyde does (p. 582), forming the cyanohydrin $CH_2OH{\cdot}[CHOH]_3{\cdot}CH(OH){\cdot}CN$, which by hydrolysis yields *l*-mannonic acid, the CN becoming COOH as usual. Again, by oxidising *d*-gluconic acid with H_2O_2 in presence of ferric acetate it yields *d*-arabinose ; or by treating *d*-glucoseoxime, $CH_2OH[CHOH]_4{\cdot}CH : N(OH)$ with acetic anhydride and sodium acetate, it yields a pentacetyl derivative which becomes *d*-arabinose when treated with HCl.

530. **Constitution of the Glucoses.**—The molecular weight of many of the sugars has been settled by Raoult's method (p. 319). That the hexoses (the same arguments apply to the pentoses) are alcoholic aldehydes or ketones is shown by the following reactions :

When heated with acetic anhydride and sodium acetate the hexoses yield pentacetyl-derivatives, $C_6H_7O(OCH_3CO)_5$, showing that they contain 5 alcoholic hydroxyl groups (p. 578) and are pentahydric alcohols. Five out of the six atoms of oxygen are thus disposed of : that the sixth must be present either as an aldehyde or as a ketone group, is shown by the fact that these sugars give a number of the reactions which characterise aldehydes and ketones. In the aldohexoses this remaining oxygen atom must be present as an aldehyde group, for on oxidation these sugars *yield acids containing the same number of carbon atoms*, which would not be the case if the sugars were ketones (p. 624). Thus, the dextroses yield first gluconic acids, $CH_2OH{\cdot}[CHOH]_4{\cdot}CO_2H$, and then, by further oxidation, saccharic acids, $CO_2H{\cdot}[CHOH]_4{\cdot}CO_2H$; the mannoses yield mannonic acids and manno-saccharic acids, stereo-isomeric with the above acids ; whilst the galactoses yield galactonic and mucic acids, also stereo-isomeric with the preceding acids. Moreover, when reduced by sodium amalgam these sugars yield hexahydric alcohols ; *e.g.*, the mannoses yield mannitols, the dextroses sorbitol, and the galactoses dulcitol. This behaviour on reduction shows that the sugars are certainly open-chain compounds, for the above-named alcohols are all convertible into normal hexane by hydriodic acid. The rule already referred to as guiding us in the interpretation of chemical constitution, namely, that one carbon atom cannot hold more than one hydroxyl group, may be applied to these sugars, when it becomes evident that the five hydroxyl groups must be attached to five separate carbon atoms, forming one primary and four secondary alcohol groups ; the sixth carbon atom may constitute the aldehydic carbon.

The ketonic character of the ketohexoses follows from the fact that *when oxidised they yield two acids* (p. 624). Thus, the lævuloses yield trihydroxybutyric acids, $CH_2OH{\cdot}[CHOH]_2{\cdot}CO_2H$, and glycollic acid, $CH_2OH{\cdot}CO_2H$. By reduction, these sugars yield mannitol. The position of the ketone group in the open-chain representing the lævuloses may be said to be settled by the following facts. When lævulose is treated with HCN it yields a cyano-hydrin which is almost certain to contain the group :C(OH)(CN) in place of the group :CO (p. 582) ; when this cyano-hydrin is hydrolysed it yields a corresponding carboxylic acid which is equally certain to contain the group :C(OH)(COOH) ; when this acid is reduced by hydriodic acid, it yields methylbutylacetic acid, the structure of which shows that the carbonyl carbon of the original lævulose must have had one carbon atom attached to it on the one hand and four carbon atoms attached to it on the other hand. The following equations will make this apparent :

(1) $CH_2OH\cdot[CHOH]_3\cdot CO\cdot CH_2OH + HCN = CH_2OH\cdot[CHOH]_3\cdot C(OH)(CN)\cdot CH_2OH$

(2) $CH_2OH\cdot[CHOH]_3\cdot C(OH)(CN)\cdot CH_2OH + 2HOH =$
$CH_2OH\cdot[CHOH]_3\cdot C(OH)(COOH)\cdot CH_2OH + NH_3$

(3) $CH_2OH\cdot[CHOH]_3\cdot C(OH)(COOH)\cdot CH_2OH + 12HI =$
$CH_3\cdot[CH_2]_3\cdot CH(COOH)\cdot CH_3 + I_{12} + 6H_2O.$

$CH_3\cdot[CH_2]_3\cdot CH(COOH)\cdot CH_3$ or $\begin{matrix} C_4H_9 \\ CH_3 \end{matrix}\!\!>\!CH\cdot COOH$ is methylbutylacetic acid.

When dextrose is submitted to a similar series of reactions it yields normal heptylic acid, $CH_3\cdot[CH_2]_4\cdot CH_2\cdot COOH$, showing that the aldehyde group is at the end of the open-chain, a position, indeed, which is the only possible one for the $\cdot C\begin{matrix} O \\ \diagup\!\!\diagdown \\ H \end{matrix}$ group.

531. Reference must now be made to the stereoisomerism of compounds containing a number of asymmetric carbon atoms, as do these polyhydroxy-alcohols, aldehydes, ketones and acids.

It was shown at p. 621, that a compound containing two asymmetric carbon atoms can exist in four stereo-chemical modifications, when, as in the case of tartaric acid, each carbon atom is attached to the same groups, that is, when the compound is of the type *abc*C—C*abc*. Two of these are optically active, one inactive, by internal compensation and one inactive by external compensation.

In the case of a compound of the type *abc*C—C*a'b'c'* there can be no inactivity by internal compensation. A little reflection will show that, instead, there will be four optically active isomerides, one in which *abc* and *a'b'c'* are both arranged to cause dextro-rotation, one in which they are both arranged to cause lævo-rotation, and two in which they are oppositely arranged. In addition there will be two externally compensated, inactive forms.

Now the pentahydric alcohols, $CH_2OH\cdot$**C**$\,HOH\cdot CHOH\cdot$**C**$\,HOH\cdot CH_2OH$, and the corresponding dicarboxylic acids, have two asymmetric carbon atoms (printed in heavy type) and are of the form *abc*C—C*abc*. Hence, like tartaric acid, they occur in a *d*-form, an *l*-form, an externally compensated or *d* + *l*-form, and an internally compensated or *i*-form. There is, however, a fifth, viz., a second internally compensated form; for although the central carbon atom is not asymmetric, being balanced on either side, it has an H and an OH attached to it, the positions of which may be reversed.

The aldopentoses, $CH_2OH\cdot$**C**$\,HOH\cdot$**C**$\,HOH\cdot$**C**$\,HOH\cdot CHO$, and the corresponding monocarboxylic acids, $CH_2OH[CHOH]_3COOH$, have 3 asymmetric carbon atoms. Each of these should give rise to a + and a − form, and since the nature of the whole compound will depend on which carbon atoms have their attached groups in the + form, and which have them in the − form, there should be as many aldopentoses as there are ways of writing + or − three times, *e.g.*, + + +, − − −, + − +, − + −, and so on. This number is eight, so that there are 8 optically active isomerides. As the aldopentoses are of the type *abc*C—C*a'b'c'*, there are no internally compensated forms, but by combining pairs of the optically active forms, four racemic or externally compensated forms are possible.

The hexahydric alcohols, $CH_2OH\cdot$**C**$\,HOH\cdot$**C**$\,HOH\cdot$**C**$\,HOH\cdot$**C**$\,HOH\cdot CH_2OH$, and corresponding dicarboxylic acids, have four asymmetric carbon atoms, so that the number of optically active isomerides, should be discoverable by finding the number of ways of writing + and − four times. This will be found to be 16. But these alcohols are of the type *abc*C—C*abc*, wherefore those forms in which the + and − are similarly arranged, but in opposite order, *e.g.*, + − + −, − + − +, are identical, reducing the essentially different ways of writing + and − to 10, two of which represent internally compensated molecules, leaving 8 active isomerides. In addition there should be four racemic forms.

Now the aldohexose formula, $CH_2OH\cdot$**C**$\,HOH\cdot$**C**$\,HOH\cdot$**C**$\,HOH\cdot$**C**$\,HOH\cdot CHO$, also contains four asymmetric carbon atoms, and is of the type *abc*C—C*a'b'c'*, so that all 16 isomerides exist, none of which is internally compensated. Besides these there should be 8 racemic forms. At present 11 of the optically active forms are known, viz., *d*- and *l*-mannose, *d*- and *l*-glucose, *d*- and *l*-gulose, *d*- and *l*-galactose, *d*- and *l*-idose, and *d*-talose.

The ketohexoses, $CH_2OH\cdot$**C**$\,HOH\cdot$**C**$\,HOH\cdot$**C**$\,HOH\cdot CO\cdot CH_2OH$, contain 3 asymmetric carbon atoms and are of the type *abc*C—C*a'b'c'*; stereoisomerism among them, therefore, is similar to that among the aldopentoses.

It has been found to be possible to orientate those carbon atoms which have a + arrangement of groups and those which have a − arrangement in the glucoses, but for a description of the arguments employed, the student must be referred to the chemical dictionaries.

532. **The Disaccharides.**—The members of this class of sugars are characterised by being converted by hydrolysis into two molecules of glucoses (hence the synonym, *saccharo-bioses*).*

Cane-sugar or sucrose, $C_{12}H_{22}O_{11}$, is not found only in the sugar-cane, but in many other plants, such as beetroot, sorghum, maize, barley, almonds, walnuts, hazel-nuts, coffee-beans, and madder root. It occurs also in the sap of the maple, lime, birch, and sycamore, as well as in the juices of many fruits; in these, it is generally accompanied by invert-sugar (*v.i.*). During the early period of vegetation, it appears that grape-sugar and fruit-sugar are formed, and that these become cane-sugar during the ripening. The green sugar-cane contains much dextrose and lævulose, which are afterwards converted into sucrose. *Honey* contains cane-sugar and invert-sugar, in varying proportions, depending on the food of the bees.

To extract sugar from plants, they should be cut up, dried at a temperature not exceeding 100° C., and boiled repeatedly with alcohol of sp. gr. 0.87, which deposits the sugar in crystals, on cooling.

On the large scale, sugar is manufactured by crushing the cane between rollers, when an acid juice is obtained, containing about 20 per cent. of sucrose; this is neutralised by lime, to prevent inversion of the sugar, and heated to coagulate the albumin. This is skimmed off the surface, and the syrup is evaporated till it is strong enough to crystallise. About half the sugar is thus obtained in brown crystals (*moist sugar*), the remainder being partly extracted as an inferior sugar (*foots sugar*) by another evaporation, and partly left as uncrystallisable sugar in the *molasses* or *treacle*. To *refine* the raw sugar, it is dissolved in water, decolorised by filtering through a thick bed of animal charcoal, and evaporated at 60° C. (140° F.) in a copper *vacuum-pan* connected with an air-pump, since a higher temperature would invert the sugar. It may then be obtained in large crystals, *sugar-candy*, or, by stirring, in minute crystals which are drained in conical moulds, and washed with a saturated solution of sugar till they form white *loaf-sugar*.

Sugar is extracted by a similar process from the juice of the white beetroot. The juice contains about 10 per cent. of sugar, about half of which is obtained in a crystallised state.

A larger yield of crystallisable sugar has been obtained from cane and beet juice by the *strontia process*, which consists in precipitating the sugar from the boiling solution by adding strontium hydroxide; the precipitate, $C_{12}H_{22}O_{11}(SrO)_2$ is washed with hot water, and afterwards suspended in boiling water and allowed to cool, when most of the strontia is deposited as hydroxide, and the remainder is precipitated from the solution by CO_2.

Sometimes the potassium salts which are present in the molasses, and hinder crystallisation, are precipitated in the form of alum by adding aluminium sulphate.

533. *Properties of Sucrose.*—It crystallises in monoclinic prisms, which are insoluble in absolute alcohol, but dissolve to almost any extent in boiling water. 100 parts of saturated syrup at 20° C. contain 67 of sugar; the solution of sugar is dextro-rotatory. When boiled with dilute acids it is hydrolysed to a mixture of equal weights of dextrose (*d*-glucose) and lævulose (*d*-fructose), $C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6$.

* In one system of nomenclature, they are termed *dipentons*, *dihexons*, &c., according as the glucoses produced by the hydrolysis are pentoses or hexoses. Thus, *arabinon*, $C_{10}H_{18}O_9$ (from gum), is a dipenton, since it yields two molecules of arabinose by hydrolysis; cane-sugar is a dihexon, since it yields dextrose and lævulose by hydrolysis.

This mixture is known as *invert-sugar*, since it is lævo-rotatory (the lævo-rotation of lævulose being greater than the dextro-rotation of dextrose). It is prepared for the use of brewers (see foot-note, p. 726). Sucrose fuses at 160° C. (320° F.), and does not crystallise on cooling. If kept melted for some time, it is converted into a mixture of dextrose and *lævulosan*; $C_{12}H_{22}O_{11} = C_6H_{12}O_6 + C_6H_{10}O_5$. If this be dissolved in water, and yeast added, the dextrose ferments, but the lævulosan is unaltered. When further heated, but below 190° C. (374° F.), sucrose loses $2H_2O$ and becomes brown, yielding *caramelan*, $C_{12}H_{18}O_9$, an amorphous, brittle, very deliquescent body, colourless when pure, and not capable of reconversion into sugar. Commercial *caramel*, used for colouring liquids, is a mixture of this with other bodies formed at higher temperatures, and is usually made by heating starch-sugar. It is bitter. Cane-sugar does not reduce Fehling's solution unless boiled with it sufficiently long to effect the inversion of the sugar.

When sugar is melted in a little water (barley-water was formerly used), it cools to a glassy mass (*barley-sugar*) enclosing a little water; this dissolves some of the sugar and deposits it in crystals, until in course of time the whole mass is opaque and crystalline. Heated with water at 160° C., sucrose yields formic acid, carbon dioxide, and charcoal. At 280° C. some pyrocatechin is produced. Dilute acids, even carbonic, convert sucrose into dextrose and lævulose, slowly in the cold, and quickly on heating.

Fused with potash, sucrose gives the potassium-salts of oxalic, formic, acetic, and propionic acids, together with acetone.

Sucrose acts as a reducing-agent; if ammonio-nitrate of silver is added to its solution, followed by sodium hydroxide, a mirror of silver is deposited on heating. The antiseptic properties of sucrose are well known: a strong syrup arrests fermentation. Weak solution of sucrose, in contact with yeast, is first converted into dextrose and lævulose, and then into alcohol and carbon dioxide (see p. 562). Sugar absorbs ammonia gas, forming $C_{12}H_{21}(NH_4)O_{11}$, which decomposes again on exposure to air.

Sucrose behaves like a weak acid to strong bases. *Sodium sucrate*, $C_{12}H_{21}NaO_{11}$, is precipitated when strong caustic soda is added to an alcoholic solution of sugar. Slaked lime is easily dissolved by solution of sugar; if equal molecules of sugar and lime be dissolved in cold water, and alcohol added, a precipitate of $CaO.C_{12}H_{22}O_{11}$, is obtained, but if an excess of lime be employed, the precipitate is $2CaO.C_{12}H_{22}O_{11}$. When the solution of either of these is boiled, it deposits $3CaO.C_{12}H_{22}O_{11}$, which requires more than 100 parts of cold water and 200 parts of boiling water to dissolve it, but dissolves readily in solution of sugar. All these compounds are decomposed by CO_2.

If strontium hydroxide be added to a boiling solution containing 15 per cent. of sucrose, the compound $2SrO.C_{12}H_{22}O_{11}$, separates as a granular precipitate, and when 2.5 molecular weights of the hydroxide have been added, the precipitation of the sugar is nearly complete. If the precipitate be stirred with boiling water, it decomposes, on cooling, forming sugar and strontium hydroxide.

Iron is much corroded by sugar, in the presence of air, the metal being dissolved as *ferrous sucrate*, $C_{12}H_{20}Fe''O_{11}$ (?), which, in contact with air and moisture, deposits ferric hydroxide, and is reconverted into sugar, which attacks a fresh portion of the iron. Lead is also attacked and dissolved by sugar solution, especially when heated. On boiling lead hydroxide with solution of sugar, it is dissolved, and, as the solution cools, it deposits *diplumbic sucrate*, $C_{12}H_{18}Pb_2O_{11}.Aq.$, as a white powder, which loses its water at 100° C. The sugar may be completely precipitated in this form. *Triplumbic sucrate*, $C_{12}H_{16}Pb_3O_{11}$, is precipitated when soda is added to a mixture of solutions of lead acetate and sugar; it may be crystallised in needles from sugar solution.

Many metallic oxides form compounds with sugar which are readily soluble in alkalies, so that the addition of sugar to solutions of copper and iron, for example, prevents their precipitation by alkalies. If solution of sucrose be mixed with cupric sulphate, and potash gradually added, a blue precipitate of $Cu(OH)_2$ is formed, which dissolves, when more potash is added, to a deep-blue liquid, which may be

heated to boiling without change, but if long boiled or kept, deposits cuprous oxide or hydroxide as a red or yellow precipitate.

When a solution containing sugar with one-fourth of its weight of common salt is allowed to evaporate spontaneously, it deposits deliquescent rhombic prisms of $C_{12}H_{22}O_{11}.NaCl.2Aq$.

Strong sulphuric acid converts dry sucrose into a brown mass, but if water be present, or if heat be applied, the mixture froths up and blackens, evolving CO, CO_2, and SO_2 gases. Dilute sulphuric and hydrochloric acids, when boiled with sugar, convert it into a brown substance, partly soluble in alkalies, and containing about 63 per cent. of carbon (sugar contains 42). Formic acid (containing only 26 per cent. of carbon) is found in the solution. Strong nitric acid dissolves sucrose, and converts it, on heating, into oxalic and saccharic acids. When heated with dilute nitric acid, it yields, besides these, acetic, tartaric, hydrocyanic, and carbonic acids, with evolution of N, NO, and N_2O_3. A cold mixture of strong nitric and sulphuric acids converts sugar into a resinous mass, which is insoluble in water and soluble in alcohol. It explodes when heated or struck, and appears to be *sucro-tetra-nitrate*, $C_{12}H_{18}O_7(NO_3)_4$.

534. **Milk-sugar** or **lactose** (*lactobiose*), $C_{12}H_{22}O_{11} + H_2O$, is prepared by evaporating the whey of milk to a syrup, and setting it aside in a cold place to crystallise. The commercial product is generally crystallised round strings or slender wooden rods. It is purified by dissolving it in water and precipitating by alcohol. The crystals lose their water of crystallisation at 130° C. Lactose is much less sweet and less soluble than sucrose, requiring 6 parts of cold and 2.5 parts of hot water. It is insoluble in alcohol and ether. By rapidly boiling the aqueous solution, lactose may be obtained in anhydrous crystals, which dissolve in 3 parts of cold water, but quickly deposit in the hydrated form. Cow's milk contains about 4.7 per cent. of milk-sugar.

Lactose is a much stronger reducing-agent than sucrose, and precipitates cuprous oxide when gently heated with alkaline cupric solution; a fine mirror of silver is deposited when silver nitrate is mixed with ammonia, potash, and lactose, and gently warmed. Milk-sugar also differs from cane-sugar in becoming brown when heated with potash. It is dextro-rotatory and shows bi-rotation. When boiled with diluted acids, it is hydrolysed to dextrose (*d*-glucose) and galactose. Yeast causes a similar change, subsequently fermenting the dextrose to alcohol (as in *koumiss*). Putrefaction-ferments, such as old cheese, ferment milk-sugar to lactic acid (see p. 603). It is unchanged by heating to 100° C. with solution of oxalic acid, which inverts sucrose. When oxidised by nitric acid, it yields mucic and saccharic acids. By reduction with sodium-amalgam, lactose yields mannite, dulcite, isopropyl alcohol, and secondary hexyl alcohol. In its behaviour with bases milk-sugar resembles cane-sugar.

Maltose, $C_{12}H_{22}O_{11} + H_2O$, is formed by the action of malt upon starch, and was formerly mistaken for dextrose, but it is less soluble in alcohol, more dextro-rotatory, and does not reduce a weak acetic solution of cupric acetate. To prepare maltose, starch (100 parts) is ground up with water (450 parts) and gelatinised by heating on a water-bath; after cooling, crushed malt (7 parts) is added, and the mixture kept at about 65° C. (149° F.) for an hour. The malt (germinated barley) contains an albuminoid substance termed *diastase*, which acts like a ferment upon the starch, causing it to undergo hydrolysis into maltose and dextrin—

$$3C_6H_{10}O_5\ (starch) + H_2O = C_{12}H_{22}O_{11}\ (maltose) + C_6H_{10}O_5\ (dextrin).$$

The mixture, which has now become much more liquid, is boiled, filtered, evaporated to a syrup on a water-bath, and boiled with alcohol, which leaves the dextrin undissolved, and, on standing for some days, deposits the maltose in crusts of fine needles, which become anhydrous at 100° C. Maltose is easily fermented by yeast, yielding alcohol and carbon dioxide; $C_{12}H_{22}O_{11} + H_2O = 4C_2H_6O + 4CO_2$. Boiling with dilute acids converts it into glucose; $C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6$. It reduces the alkaline cupric solution when warmed, but not the acetic solution.

Trehalose, or *mycose*, $C_{12}H_{22}O_{11} + 2H_2O$, is found in the *trehala manna*, or *nest-sugar*, of Persia, an edible substance produced by an insect from the tree on which it lives. It is also found in the *ergot* of rye and in certain edible fungi, whence its name of mycose. Alcohol extracts it from the manna. It crystallises in prisms which have a sweet taste, and fuses at 100° C., losing their water at 130° C. It is soluble in water and in hot alcohol, but not in ether. It is more strongly dextro-rotatory than cane-sugar.

535. The constitution of the disaccharides is not yet known; all that can be said is that they are probably anhydrides formed from two molecules of glucoses, since they break up into these by absorption of water. The two molecules may be of the same glucose (as in the case of maltose) or of different glucoses (as in the case of cane-sugar). Cane-sugar and milk-sugar yield octacetyl-derivatives when treated with acetic anhydride and sodium acetate, showing that they are octohydric alcohols. It will be noticed that maltose is the only disaccharide which is directly fermentable with yeast and directly reduces Fehling's solution. Maltose and lactose yield osazones, showing that they are aldehydic.

536. **Trisaccharides.**—These yield three molecules of hexoses when hydrolysed. *Raffinose*, or *melitose*, $C_{18}H_{32}O_{16} + 5H_2O$, is the chief constituent of *Australian manna*, an exudation from *Eucalyptus mannifera*, and occurs in cotton seeds and sugar-beets. It crystallises in fine needles. It is but slightly sweet, and dissolves in water and alcohol. Melitose does not reduce alkaline cupric solution, and is dextro-rotatory. Diluted acids and yeast convert it into *d*-fructose and *melibiose*, $C_{12}H_{22}O_{11}$, which subsequently breaks up into dextrose and galactose.

Melezitose, $C_{18}H_{32}O_{16} + 2H_2O$, is extracted by alcohol from the manna exuding from the larch. Its crystals lose H_2O at 100° C. and are sweet enough to be used as a substitute for sugar. It does not easily reduce alkaline cupric solution, and is dextro-rotatory. It is converted, though not easily, into dextrose by boiling with dilute acids.

The Starches and Celluloses (Polysaccharides).

537. **Starch**, or *amylose*, $(C_6H_{10}O_5)_n$, differs from the sugars in being insoluble in cold water, and therefore tasteless, and in not forming crystals, but having an *organised* structure visible under the microscope, which is not seen in any artificial product of the laboratory. It is an indispensable constituent of all plants (except fungi), and is stored up in their seeds and tubers, for the nourishment of the young shoots.

To obtain starch on the small scale, flour (which contains about 60 per cent.) is mixed with cold water to a stiff *dough*, which is tied up in fine muslin and well kneaded in a basin of distilled water, when the grains of starch pass through, leaving the tenacious *gluten* in the muslin. The milky fluid is left to settle for a few hours, the bulk of the water poured off, the starch collected on a filter, and dried by exposure to air.

On the large scale, in England, starch is commonly made from rice, which contains about 80 per cent. The rice is soaked for 24 hours in water containing about 0.3 per cent. of caustic soda; it is then washed, ground into flour, and again soaked for two or three days in a fresh alkaline solution; the starch is allowed to settle, and the alkaline liquid, holding the gluten in solution, is drawn off.* The

* The gluten is sometimes precipitated by sulphuric acid, and used as a feeding-stuff.

starch is then stirred up with water, the heavier woody fibre allowed to subside, and the milky liquid run off into another vessel, where it deposits the starch. This is transferred to drainers, where it partly dries, and the drying is finished by gradual application of heat; this splits the starch into roughly prismatic fragments, which still retain about 18 per cent. of water. Commercial starch is generally coloured blue by a little ultramarine or smalt, in order to correct the yellow tint of linen.

Being possessed of an organised structure, starch varies in external aspect, according to the plant from which it is obtained. When powdered starch is examined by the microscope, it appears in grains resembling some of those in Fig. 283: the largest are those of potato-starch (P), about $\frac{1}{300}$ inch in the longer diameter; the smallest are those of rice (R), about $\frac{1}{3000}$ inch in diameter: wheat-starch (W) has nearly spherical granules, $\frac{1}{1000}$ inch in diameter; (A) is the starch of *arrowroot*, from *Maranta arundinacea*, a tropical plant. When

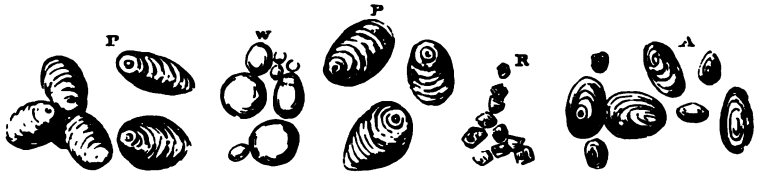


Fig. 283.

moistened with water and viewed under a microscope, provided with a polariser and analyser, starch granules behave like doubly refracting crystals, exhibiting a black cross when the planes of polarisation of the polariser and analyser are at right angles, which becomes white when the analyser is turned through an angle of 90°; this is best seen in the starch of potato, Indian corn, and *tous le mois* (from *Canna coccinea* of the Arrowroot order). The starch granules are composed externally of *starch cellulose*, or *farinose*, and internally of *granulose*, and, perhaps, other isomeric bodies.

Cold water does not attack starch, unless the cell-walls are broken by trituration, when a part of the granulose dissolves, yielding a solution strongly dextro-rotatory and coloured blue by iodine, which gives a violet colour to farinose. When starch is heated with water to about 50° C., the granules begin to burst, which is completed at about 70° C.; the granulose then dissolves to a viscous liquid, becoming a jelly on cooling and a gummy mass when dried. The cell-wall may be dissolved in the cold by strong alkalies, acids, and zinc chloride. Heated with glycerine at 190° C., starch is dissolved, and if the solution be mixed with alcohol, *soluble starch* is precipitated, and, while moist, may be dissolved by water or weak alcohol. Its strong aqueous solution becomes a jelly on standing.

The conversion of starch into maltose and dextrin by the action of diastase has already been mentioned. Other enzymes, notably the *ptyalin* of the saliva, effect a similar change.

The aqueous solution of starch is precipitated by alcohol, by baryta and lime, and by ammoniacal lead acetate, which gives $C_6H_{10}O_5.PbO$. For the behaviour of starch with iodine, see p. 194. When boiled with diluted sulphuric or hydrochloric acid, starch is converted into *d*-glucose, maltose and dextrin (p. 726).

When starch is heated with acetic anhydride, it yields an insoluble compound,

which may be represented as $C_{12}H_{14}O_4(C_2H_3O_2)_6$. This yields starch and potassium acetate when saponified by potash, showing that starch is a hexahydric alcohol, $C_{12}H_{14}O_4(OH)_6$. Strong sulphuric acid dissolves starch in the cold, apparently forming a soluble sulpho-acid. When heated, carbonisation occurs.

Heated at about 205° C. for some hours, starch becomes brownish and soluble in cold water, having been converted into the isomeric compound dextrin. This conversion of starch into a soluble form is important in the preparation of food. In toasting bread a portion of the starch becomes dextrin, which is dissolved in toast and water. Further heated, starch is carbonised and yields products of destructive distillation resembling those from sugar.

538. **Dextrin,** or *British gum*, $C_6H_{10}O_5$, is prepared by moistening starch with one-third of its weight of weak nitric acid (0.66 per cent.), drying it in air, and heating to 115° C. There are several varieties, *e.g.*, *erythro-dextrin*, coloured red by iodine-water: and *achro-dextrin*, not coloured by iodine. The erythro-dextrin is formed at first when starch is boiled with diluted sulphuric acid, so that the blue starch-reaction with iodine gives place to a red, and finally ceases. Commercial dextrin gives a violet colour with iodine, because it contains unaltered starch and erythro-dextrin; it is sweet from the presence of glucose. It may be purified by dissolving in water and precipitating by alcohol.

Dextrin dissolves when soaked in water, and is left on evaporation as a transparent mass. Its solution has twice the dextro-rotatory power of dextrose. Pure dextrin does not reduce Fehling's solution; commercial dextrin does, though not so quickly as glucose. It shows aldehydic properties, and when boiled with dilute H_2SO_4, or HCl, it is converted into dextrose. Nitric acid oxidises it to oxalic acid, while ordinary gum yields mucic acid. Heated with acetic anhydride, it yields an acetyl-compound isomeric with that from starch (see above), which is converted into the dextrin-derivative at 160° C. Dextrin is used by calico-printers for thickening their colours; it is used for adhesive stamps, for confectionery, and for stiffening surgical bandages.

Inulin, $(C_6H_{10}O_5)_6.H_2O$, was first obtained from elecampane root (*Inula helenium*), an aromatic medicinal plant. It is also found in the roots of the dahlia, and in the Jerusalem artichoke, which belong to the same sub-order (*Corymbiferæ*), and in the roots of dandelion and chicory, belonging to the *Cichoraceæ*; all being plants of the natural order *Compositæ*. It may be extracted from dahlia roots, which contain 10 per cent., by boiling with water, which deposits the inulin in minute spheres on cooling. It is not coloured blue by iodine, and does not reduce Fehling's solution. It is insoluble in alcohol. Solution of inulin is lævo-rotatory. When boiled with dilute sulphuric acid, it yields lævulose. It also differs from starch in being unchanged by diastase. It melts at 160° C.

Glycogen, or *animal starch*, $(C_6H_{10}O_5)_n$, occurs in the liver, blood, flesh, yolk of egg, and oysters, where it is said to amount to 9.5 per cent. of the dried fish. It is most abundant in the liver during active digestion, and disappears quickly after death, being converted into dextrose by fermentation. To prepare glycogen, the minced liver is extracted with water as long as it runs off milky: the albumin is coagulated by boiling, and the filtrate mixed with alcohol, which precipitates the glycogen: it is purified by boiling with weak acetic acid to remove albuminoids, again precipitating with alcohol, and washing with ether to remove traces of fat. When dried over $CaCl_2$, glycogen has the formula $(C_6H_{10}O_5)_3.H_2O$; it loses the H_2O at 100° C. It is an amorphous powder like starch, swelling in water, and yielding a turbid solution on heating. The solution is strongly dextro-rotatory, and gives a wine-red colour with iodine. Glycogen does not reduce Fehling's solution, and is not fermented by yeast. Diastase converts it into maltose and dextrin, as it does starch (p. 733). It is converted into dextrose when boiled with dilute H_2SO_4 or HCl, or when placed in contact with saliva or pancreatic juice.

539. **Gums.**—The carbohydrates of this group resemble dextrin in yielding viscous solutions in water, in being precipitated by alcohol, and

in conversion into sugars by boiling with dilute acids: but the gums have a marked acid tendency, though they do not form well-defined salts. Moreover, the gums yield mucic acid when oxidised by nitric acid.

Arabin, or *arabic acid*, $2C_6H_{10}O_5 + H_2O$, occurs in *gum arabic*, an exudation from various tropical acacias. It is extracted by dissolving the gum in water, acidifying with HCl, and adding alcohol, which precipitates it in white flakes; or the acid solution may be dialysed (p. 278), when the aqueous solution of arabin remains in the dialyser. The pure aqueous solution is not precipitated by alcohol, but the presence of a minute quantity of a base or a salt determines the precipitation. The aqueous solution has an acid reaction, and, on evaporation, leaves a vitreous mass, which loses water above 120° C., yielding *metarabin* isomeric with dextrin. This does not dissolve in water, but increases greatly in bulk. Arabic acid decomposes alkali carbonates, and the composition of its salts indicates the formula $C_{24}H_{36}O_{24}$ or $H_2C_{36}H_{54}O_{27}$. It appears to occur in gum arabic as arabates of calcium, magnesium, and potassium, since, when incinerated, the gum leaves about 3 per cent. of ash containing those metals.

Arabin gives a characteristic reaction with $CuSO_4$, followed by KOH, which produces a blue precipitate, insoluble in excess, and neither blackened nor reduced by boiling, but collecting into a blue mass, leaving the liquid colourless. When arabin is boiled with dilute H_2SO_4 it is converted into *arabinose* or *gum-sugar*, $C_5H_{10}O_5$ (p. 725); substances which yield pentoses on hydrolysis are known as *pentosans*.

Gum Senegal, obtained from similar sources, is used by calico-printers to thicken their colours. It is darker in colour than gum arabic, but also consists essentially of arabin.

Metarabin, or *cerasin*, $C_{12}H_{20}O_{10}$, is found in the gum of the cherry-tree and beech-tree (*wood-gum*), probably as calcium metarabate, which remains undissolved after the calcium arabate which accompanies it has been extracted by water; when heated with lime-water, it is converted into calcium arabate, which dissolves. It is also found in the residue of beet-root from which the juice has been expressed. By hydrolysis it yields xylose (p. 725), and is therefore a pentosan.

Bassorin, very similar to cerasin, occurs in *Bassora gum* and in *gum tragacanth*, the exudation from *Astragalus tragacantha*, a Papilionaceous plant. These gums do not dissolve in water like gum arabic, but swell up immensely by absorption of water, and form a *mucilage*. When boiled with dilute acids it is converted into dextrose. A substance very similar to bassorin is formed in the *ropy* or *viscous fermentation* of saccharine liquids. The mucilaginous liquids obtained by boiling linseed (*linseed tea*), quince-seed, and marshmallow root with water, contain bassorin, or some allied body.

Gelose, or *parabin*, $C_{12}H_{22}O_{11}$, forms the greater part of Ceylon moss (*Gracilaria lichenoides*) and China moss (*G. spinosa*), sea-weeds which are used for making soups and jellies. Carrots and beet also contain gelose. When dissolved in as much as 500 parts of hot water, it sets to a jelly on cooling. It also differs from the other bodies of this group by dissolving in dilute acids and being precipitated by alkalies. When long heated with alkalies it is converted into arabin. It does not appear to yield a sugar when boiled with dilute acids.

540. **Cellulose**, $(C_6H_{10}O_5)_{12}$, is the substance which composes the walls of plant-cells, and is left undissolved after the matters contained in and encrusting the cells have been removed by various solvents. Hence, white filter-paper, prepared cotton-wool, and well-washed linen consist of nearly pure cellulose. To purify these they are digested successively with dilute KOH, dilute HCl, water, alcohol, and ether; the encrusting substances of the cellulose are thus removed.

When pure, cellulose is white, opaque, exhibits an organised structure, is infusible and insoluble in all ordinary solvents. It may be dissolved

by *Schweitzer's reagent*, a solution of cupric hydroxide in ammonia. The cellulose is precipitated in flakes on addition of an acid. When contact with the Schweitzer's reagent is sufficiently brief to attack the superficial fibres only, and the cellulose fabric is then pressed and dried, it becomes impervious to water; in this way the green waterproof coverings known as *Willesden paper* are manufactured. Chlorine, in presence of moisture, slowly attacks cellulose, so that paper becomes brittle if the excess of bleach be not *killed* by an antichlore (p. 221). Iodine does not give a blue colour with pure cellulose, but the cellular tissue of plants is often blued by it, from the presence of a little starch. Ferric oxide slowly oxidises cellulose, and, since the ferrous oxide is repeatedly oxidised again, a continual oxidation and corrosion of the cellulose is kept up, as may be seen from the effect of *iron-mould* on linen and of rusty nails on wood.

Strong sulphuric acid converts dry cellulose into a gummy mass which dissolves in the acid with very little colour in the cold. If this solution be immediately poured into water, it yields a gelatinous precipitate, but after digestion for some hours with the acid, a clear solution is formed in water, and if this be largely diluted and boiled, the cellulose is converted, first into dextrin, and then into dextrose, which may be obtained as a syrup by neutralising the acid liquid with chalk, filtering, and evaporating. By fermenting this dextrose, the curious transformation of rags into alcohol may be accomplished. Cotton-wool dissolves in a mixture of sulphuric acid with one-fourth its weight of water, and, on dilution, a precipitate of *amyloid* is obtained, which is isomeric with cellulose, but is coloured a fugitive blue by iodine.

By immersing unsized paper in a cold mixture of strong sulphuric acid with half its volume of water, it becomes converted externally into amyloid. This is turned to account for making *vegetable parchment*, which is five times as strong as paper, and is waterproof. After immersion in the acid, the paper is thoroughly washed with water and finally with weak ammonia. A strong solution of zinc chloride affects the paper in the same way. The *parchment paper* is translucent; it may be boiled in water without disintegration; it receives many useful applications, as for luggage labels which are not easily torn or destroyed by rain, as a substitute for bladder in tying over preserves, &c., and for making dialysers.

When cellulose is left for twelve hours in H_2SO_4 of sp. gr. 1.453, or in HCl of sp. gr. 1.16, it is converted into a brittle mass of *hydro-cellulose*, $C_{12}H_{22}O_{11}$(?), which is more easily oxidised than cellulose, and dissolves in hot potash. This is applied for dissolving the cotton from old fabrics containing wool, the latter being left as *shoddy*. *Dry rot* is ascribed to a similar change in the wood caused by acid substances generated in its fermentation.

Cellulose swells up and becomes gummy when in contact with strong potash or soda; on heating to 160° C. with strong potash, it dissolves, and the solution when acidified, yields a precipitate isomeric with cellulose, but easily soluble in alkalies. If calico be soaked for half an hour in very strong potash or soda, and washed with alcohol, it is converted into $C_{12}H_{20}K_2O_{11}$, or $C_{12}H_{20}Na_2O_{11}$ (*mercerisation*). Both compounds are decomposed by CO_2. When treated with CS_2 they form thio-carbonates which are soluble in water; the solution coagulates spontaneously, and immediately on the addition of salt solution, the coagulum being regenerated cellulose. *Viscose* is the viscid solution of these thiocarbonates, and is applied for producing a glaze of cellulose on fabrics. When cellulose is boiled with

potash of sp. gr. 1.5 it dissolves to a brown solution which deposits brown flakes (*ulmic acid*) when acidified; but on prolonged heating, the colour disappears, and carbonate, oxalate, formate, and acetate of potassium are found in solution. By heating cellulose with fused potash, abundance of potassium oxalate is obtained (see *Oxalic acid*).

Cellulose was the name originally given to the constituent of plants which remains after treatment with reagents that may be supposed to remove all other constituents. It is now realised that this residue when obtained from different plants is not necessarily the same substance. Modern workers have distinguished between *cotton cellulose*, *jute cellulose*, and *straw cellulose*. The first of these is characterised by its resistance to chlorine, by the fact that it yields no furfurol when distilled with acid, and by being precipitated unchanged from its solution in a mixture of CS_2 and NaOH solution. Jute cellulose is somewhat attacked by chlorine, yields some 3–5 per cent. of furfurol when distilled with acid, and is decomposed by NaOH and CS_2. Straw cellulose absorbs a considerable proportion of chlorine, yields some 15 per cent. of furfurol, and is coloured red by aniline salts: it also is decomposed by NaOH and CS_2.

For the detection of cellulose in the microscopic examination of tissues, advantage is taken of its conversion into amyloid by zinc chloride, and of the bluing of this by iodine. The reagent is prepared by dissolving 6 per cent. of KI in solution of $ZnCl_2$ of sp. gr. 1.8, and adding as much iodine as will dissolve.

By heating cellulose with 8 parts of acetic anhydride in a sealed tube at 180° C., it may be converted into *hexacetyl cellulose*, or *cellulose hexacetate*—

$$C_{12}H_{20}O_{10} + 6(CH_3CO)_2O = C_{12}H_{10}O_4(OCH_3CO)_6 + 6(CH_3COOH).$$

Cellulosetetracetate is made by heating cellulose at 110° C. with zinc acetate solution and treating the cooled mass with acetyl chloride. It dissolves in chloroform, from which it may be obtained in films by evaporation.

Oxycellulose is the name given to the product of aldehydic nature obtained by the action of various oxidising-agents on cellulose.

541. *Action of nitric acid on cellulose.*—Cold dilute nitric acid (sp. gr. 1.2) does not act on cellulose in the form of filter-paper, and scarcely when heated to 100° C. Acid of 1.42 corrodes it, producing amyloid and malic acid, and, on boiling, suberic and oxalic acids. Cotton, linen, or paper, soaked for two or three minutes in the strongest nitric acid and washed, resembles parchment, and is waterproof and very combustible, having become partly converted into *cellulose hexanitrate*, or *pyroxylin* (*gun-cotton*); $C_{12}H_{14}O_4(OH)_6 + 6(HO\cdot NO_2) = C_{12}H_{14}O_4(O\cdot NO_2)_6 + 6HOH$. This change, which is analogous to the conversion of alcohol into the ethereal salts, is, like that conversion, much facilitated by the presence of strong sulphuric acid, which may either act simply as a dehydrating-agent or may form an intermediate sulphonic acid.

If pure dry cellulose (prepared cotton-wool) be steeped for some time in a cold mixture of equal molecular weights of the strongest nitric and sulphuric acids, and afterwards thoroughly washed, and dried by exposure to air, it has the composition of cellulose hexanitrate above given, retaining the organised structure of the original cotton, but being somewhat harsher to the touch, and becoming highly electrified when drawn through the dry hand.

Pyroxylin is insoluble in water, alcohol, and ether, either separately or mixed, but it dissolves in acetic ether and in ethereal solution of ammonia. It is not oxidised by potassium permanganate, as cellulose is, so that it may be used for filtering its solution. When moderately heated, it burns more rapidly than gunpowder, and it is detonated by the blow of a hammer or by the rapid vibration caused by a smart detonation in its vicinity. Pyroxylin dissolves in strong sulphuric acid, and the solution is not blackened by heat. Strong nitric acid also

dissolves it when heated, but it is reprecipitated by strong sulphuric acid or by water. Strong potash dissolves it with formation of potassium nitrate, nitrite, and oxalate, together with glucose and some other organic bodies. The formation of potassium nitrate would be expected if pyroxylin be a nitrate of cellulose.

Potassium hydrosulphide, in alcoholic solution, reconverts pyroxylin into cellulose, potassium nitrite being found in solution—

$$C_{12}H_{14}O_4(O{\cdot}NO_2)_6 + 6KHS = C_{12}H_{14}O_4(OH)_6 + 6KNO_2 + S_6.$$

This shows that pyroxylin is not, as was formerly supposed, the *trinitro-cellulose* $C_6H_7(NO_2)_3O_5$, since, in that case, the NO_2 group would be reduced to the NH_2 group, and an amido-compound would be formed (p. 659).

A strong aqueous solution of ferrous chloride containing HCl also converts pyroxylin into cellulose, with evolution of nitric oxide—

$$C_{12}H_{14}O_4(O{\cdot}NO_2)_6 + 12FeCl_2 + 12HCl = C_{12}H_{14}O_4(OH)_6 + 6Fe_2Cl_6 + 6NO + 6H_2O.$$

This would be the result expected from cellulose hexanitrate. Iron filings and acetic acid reduce pyroxylin to cellulose, the nascent hydrogen converting the NO_3 group into NH_3—

$$C_{12}H_{14}O_4(NO_3)_6 + H_{48} = C_{12}H_{14}O_4(OH)_6 + 6NH_3 + 12H_2O.$$

Pyroxylin behaves like a nitrate when shaken with mercury and strong sulphuric acid, evolving the whole of its nitrogen as nitric oxide.

542. The following proportions may be recommended for preparation of gun-cotton on a small scale:—Dry 1000 grains of pure nitre (p. 338) at a very moderate heat, place it in a dry retort (Fig. 73), pour upon it 10 drachms (by measure) of strong sulphuric acid, and distil until 6 drachms of nitric acid have passed over into the receiver. Dry some pure cotton-wool, and weigh out 30 grains of it. Mix 2½ measured drachms of the nitric acid with an equal volume of strong sulphuric acid in a small beaker. Allow the mixture to cool, immerse the cotton-wool in separate tufts, pressing it down with a glass rod, cover the beaker with a glass plate, and set it aside for fifteen minutes. Lift the cotton out with a glass rod, throw it into at least a pint of water, and wash it thoroughly in a stream of water till it no longer tastes acid or reddens blue litmus-paper. Dry the cotton by exposure to air or to a very moderate heat.

Gun-cotton is manufactured from the waste cuttings from spinning-machines (cotton-waste), which is first thoroughly cleansed. One part of nitric acid (sp. gr. 1.52) and 3 parts by weight (or 2.45 by volume) of sulphuric acid (sp. gr. 1.84) are placed in separate stoneware cisterns with taps, and allowed to run simultaneously, in slow streams, into another stoneware cistern furnished with a tap and an iron lid, through a second opening in which an iron stirrer is moved to mix the acids thoroughly. The mixture is set aside for several hours to become perfectly cool.

A quantity of the mixed acids is drawn off into a deep stoneware pan standing in cold water, and provided with a perforated iron shelf, upon which the cotton may be drained. The well-dried cotton is immersed, a little at a time, in the acid, and stirred about in it for two or three minutes with an iron stirrer. It is then placed upon the perforated shelf, and the excess of acid squeezed out with the stirrer. Enough acid is drawn from the cistern to make good that which has been absorbed by the cotton, and more cotton is treated in the same way. Since a considerable rise of temperature is produced by the action of the nitric acid upon the cotton, it is necessary to keep the pan surrounded with cold water. A large proportion of the cotton is doubtless converted into gun-cotton in this preliminary immersion in the mixed acids; but in order to convert the remainder, it is necessary to allow the cotton to remain in contact with the acid for a much longer period, so as to ensure its penetration into every part of the minute twisted tubes of the fibre.

The skeins are next transferred to a jar with a well-fitting cover, in which they are pressed down and completely covered with the mixed acids, of which from 10 to 15 times the weight of the cotton will be required, according to the closeness with which the skeins are packed in the jar. The jar is placed in cold water, and the cotton allowed to remain in the acid for about twelve hours.

The skeins are then removed, with the aid of an iron hook, to a centrifugal extractor, which is a cylinder made of iron gauze, through which the bulk of the

acid is whirled out by the rapid rotation of the cylinder upon an axle. In order to wash away the remainder of the acid, the cotton is plunged, suddenly, to avoid rise of temperature, into a cascade of water, and is then drained in the centrifugal extractor, and again rinsed in much water. It is next reduced to pulp in a rag-engine such as is employed in paper-mills. The pulp is thoroughly washed by being well stirred by a *poaching-engine* for about forty-eight hours in a stream of warm water, so as to remove every trace of acid, which is assisted by rendering the water alkaline with a little lime or carbonate of soda or with ammonia. The pulp is then drained, moulded into discs or any other required form, condensed by hydraulic pressure until it has at least the same specific gravity as that of water, and dried upon heated plates. As it leaves the hydraulic press, the cotton contains about one-fifth of its weight of water, so that it may, if required, be cut up or bored without danger of explosion.

543. When a mass of the gun-cotton wool is exploded in an unconfined state, the explosion is comparatively slow (though appearing to the eye almost instantaneous), since each particle is fired by the flame of that immediately adjoining it, the heated gas (or flame) escaping outwards, so that some time elapses before the interior of the mass is ignited. But when the gun-cotton is enclosed in a strong case, so that the flame from the portion first ignited is unable to escape outwards, and must spread into the interior of the mass, this is ignited simultaneously at a great number of points, and the decomposition occurs far more rapidly ; a given weight of cotton being thus consumed in a much shorter time, a far higher temperature is produced, and the ultimate results of the explosion are much less complex, as would be expected from the well-known simplifying effect of high temperatures upon chemical compounds.

If a tuft of gun-cotton wool be placed at the bottom of a tall glass cylinder and inflamed by a heated wire, it will be seen that, immediately after the explosion, the gas within the cylinder is colourless, but soon becomes red, showing that NO was present among the products, and became converted into NO_2 by the oxygen of the air. The water formed by the combustion of the hydrogen converts the NO_2 into HNO_2 and HNO_3 (p. 101), and hence the acid character of the moisture deposited in the barrel of a fowling-piece in which gun-cotton cartridges are employed. A little HCN can be detected among the products of combustion of loose gun-cotton.

Berthelot estimates the pressure produced by the detonation of gun-cotton, compressed to a density of 1.1, at 24,000 atmospheres, or about 160 tons per square inch, being only half the pressure assigned by him to the detonation of mercuric fulminate.

If a piece of compressed gun-cotton be kindled with a hot wire, it burns rapidly away, producing a large volume of flame, but without any explosive effect.* In order that gun-cotton fired in this manner might be used for destructive purposes, it was found necessary to confine it in strong cases, so that the flame of the portion first ignited should be employed in raising the temperature of the rest to the exploding-point.

The *unconfined* gun-cotton, however, can be made to explode or detonate with most destructive violence, by exploding in contact with it a *detonating fuze*, consisting of a little tube of quill or thin metal charged with a few grains of mercuric fulminate. Such detonation can be communicated along a row of pieces of compressed cotton placed at short distances from each other. This *sympathetic explosion* is by no means confined to gun-cotton, but exists in the case of nitroglycerine, and even gunpowder. The *modus operandi* of the detonating fuze appears to consist in the influence of vibratory motion, and the nature of the motion necessarily depends upon the nature of the explosive. That it is not a result of the action of heat is proved by the circumstance that wet gun-cotton may be exploded by a detonating fuze, so that torpedoes may be charged with a mixture of gun-cotton pulp and water, containing 15 per cent. of the latter, if a small charge of dry gun-cotton be placed in contact with the fuze. It has been found that the wet gun-cotton is more easily detonated when in a frozen state.

* Too much stress, however, should not be laid upon this as rendering gun-cotton magazines safer in case of fire than gunpowder magazines. The experiment with gunpowder mentioned at p. 342 shows that if all the particles of an explosive be raised at once to nearly the inflaming-point, the first particle which inflames will cause the detonation of the remainder. Since the inflaming-point of gun-cotton is low, the above condition would be easily fulfilled in a conflagration.

The very destructive effect of the gun-cotton exploded in this way is, of course, due to the sudden manner in which the whole mass is resolved into gaseous products. When heat is the cause of the explosion, it must be comparatively slow, for gun-cotton transmits heat slowly, but the vibration caused by detonation is transmitted with the velocity of sound, and the explosion becomes rapid in proportion.

544. Gun-cotton is more easily exploded than gunpowder; the latter requires a temperature of at least 600° F. (316° C.), whilst gun-cotton may explode at 277° F. (136° C.), and must explode at 400° F. (204° C.). It is very difficult to explode gunpowder by percussion, even between a steel hammer and anvil; but gun-cotton invariably detonates in this way, though the explosion is confined to the part under the hammer. The explosion of gun-cotton is approximately represented by the equation, $C_{12}H_{14}O_4(NO_3)_6 = 5CO + 7CO_2 + H_8 + 3H_2O + N_6$, and is attended by the evolution of 1071 heat-units per unit weight, but by no smoke, a most important advantage in mines, the atmosphere of which is sometimes rendered almost intolerable by the smoke of gunpowder used in blasting; but death has been caused by the carbonic oxide generated. The absence of residue from the gun-cotton prevents the fouling of guns, and renders it unnecessary to sponge them after each discharge, for the amount of incombustible mineral matter present in the cotton is very small (from 1 to 2 per cent.), and is entirely scattered by the explosion.

Nitrated cellulose is the main constituent of several modern sporting powders such as *E. C. sporting powder*, *E. C. rifle powder*, and *Schultze's powder*.

545. *Soluble pyroxylin*, or *collodion cotton*, is a mixture of cellulose nitrates lower than the hexanitrate—*e.g.*, the *penta-*, *tetra-*, *tri-*, and *di-nitrates*. It is the product of the action upon cellulose of a mixture of HNO_3 (1 mol.) and H_2SO_4 (1 mol.) slightly diluted with water ($1\frac{3}{4}$ mols.). It differs from pyroxylin in being soluble in a mixture of ether with one-seventh of alcohol, yielding a viscous solution, which leaves the transparent collodion film when evaporated. It is much less rapidly combustible than pyroxylin.

In order to prepare the soluble cotton for collodion, 3 measured ounces of ordinary HNO_3 (sp. gr. 1.429) are mixed with 2 ounces of water in a pint beaker. Nine measured ounces of strong H_2SO_4 (sp. gr. 1.839) are added to this mixture, with continual stirring. A thermometer is placed in the mixture, which is allowed to cool to 140° F.; 100 grains of dry cotton-wool, in ten separate tufts, are immersed in the mixture for five minutes, the beaker being covered with a glass plate. The acid is then poured into another beaker, the cotton squeezed with a glass rod, and thrown into a large volume of water: it is finally washed in a stream of water till it is no longer acid, and dried by exposure to air.

Collodion balloons.—These balloons may be made in the following manner:—Six grains of collodion-cotton, prepared according to the above directions, are dissolved in a mixture of 1 drachm of alcohol (sp. gr. 0.835) and 2 drachms of ether (sp. gr. 0.725) in a corked test-tube. The solution is poured into a dry Florence flask, which is then turned about slowly, so that every part of its surface may be covered with the collodion, the excess of which is then allowed to drain back into the tube. Air is then blown into the flask through a long glass tube attached to the bellows as long as any smell of ether is perceptible. A penknife blade is carefully inserted between the flask and the neck of the balloon, which is thus detached from the glass all round: a small piece of glass tubing is introduced for an inch or two into the neck of the balloon, so that the latter may cling round it. Through this tube air is drawn out by the mouth, until one-half of the balloon has left the side of the flask and collapsed upon the other half: by carefully twisting the tube, the whole of the balloon may be detached and drawn out through the neck of the flask, when it must be quickly untwisted, distended by blowing through the tube, tied with a piece of silk, and suspended in the air to dry. The average weight of such balloons is 2 grains.

Celluloid, or *artificial ivory*, or *xylonite*, used for combs, billiard-balls, &c., is essentially compressed collodion-cotton mixed with camphor and zinc oxide.

When collodion-cotton is kept for some time, especially if at all damp, it

undergoes decomposition, filling the bottle with red fumes, and becoming converted into a gummy mass, which contains oxalic acid.

546. *Tunicin*, $C_6H_{10}O_5$, or *animal cellulose*, is prepared from the outer covering or *mantle* of the mollusks belonging to the class *Tunicata*. The mantle is long boiled with hydrochloric acid and potash, in succession, and the residue washed with water, alcohol, and ether. Tunicin is left as a translucent mass, so closely resembling cellulose in properties that it is believed by some chemists to be identical with it.

XIV. GLUCOSIDES.

547. The compounds belonging to this class are capable of conversion into a sugar and some other compound by the action of acids, alkalies, and certain ferments, the change being generally the result of hydrolysis (p. 265). They are chiefly found in plants, and generally yield products of decomposition belonging to the aromatic group. Some of them have been already noticed.*

Salicin, $C_6H_{11}O_5 \cdot O \cdot C_6H_4CH_2OH$, is extracted from willow-bark (*Salix*) by boiling it in water, removing the colouring-matter and tannin from the solution by boiling with lead hydroxide, precipitating the excess of lead by H_2S, and evaporating the filtered liquid, when the salicin crystallises in needles which may be recrystallised from alcohol. It forms bitter colourless prisms (m.-p. 188° C.) soluble in about 30 parts of cold water, in less alcohol, but not in ether. It is readily distinguished by the bright red colour which it gives with strong sulphuric acid, which detects it when applied to the inner bark of the willow. With emulsin (p. 566) or saliva, its aqueous solution yields glucose and salicyl-alcohol or *saligenin:*

$$C_{13}H_{18}O_7 + H_2O = C_6H_{12}O_6 + C_6H_4(OH) \cdot CH_2 \cdot OH.$$

The saligenin gives a blue colour with ferric chloride.

Salicin is occasionally administered as a febrifuge, and is a common adulteration of quinine.

When solution of salicin is boiled for some time with dilute sulphuric or hydrochloric acid, it yields an amorphous precipitate of *saliretin*, a product of the decomposition of saligenin—

$$2C_7H_8O_2 \text{ (\textit{saligenin})} = H_2O + C_{14}H_{14}O_3 \text{ (\textit{saliretin})}.$$

Sulphuric acid and potassium dichromate convert salicin into oil of spiræa (p. 586). Fused with potash, it yields potassium salicylate. Dilute nitric acid converts salicin into *helicin:* $C_{13}H_{18}O_7 + O = C_{13}H_{16}O_7 + H_2O$. This is also a glucoside, yielding glucose and oil of spiræa when hydrolysed by ferments or acids; $C_{13}H_{16}O_7 + H_2O = C_6H_{12}O_6 + C_7H_6O_2$. Strong nitric acid converts salicin into *nitrosalicylic acid*, $C_6H_3(OH)(NO_2)CO_2H$. When acted on by chlorine, salicin yields substitution-products containing one, two, and three atoms of chlorine, and these, when boiled with dilute acids, yield the corresponding chlorosaligenins.

Populin, or *benzoyl-salicin*, $C_{13}H_{17}(C_7H_5O)O_7 + 2H_2O$, is a sweet crystalline body existing, together with salicin, in the bark and leaves of the aspen (*Populus tremula*), a tree of the Willow order, and may be extracted in the same way as salicin. When boiled with $Ba(OH)_2$, it yields salicin and benzoic acid (which becomes barium benzoate); $C_{13}H_{17}(C_7H_5O)O_7 + H_2O = C_{13}H_{18}O_7 + C_7H_5O \cdot OH$. Boiled with dilute acids, it is converted into benzoic acid, saliretin, and glucose. It is obtained artificially by fusing salicin with benzoic anhydride—

$$C_{13}H_{18}O_7 + (C_7H_5O)_2O = C_{13}H_{17}(C_7H_5O)O_7 + C_7H_5O \cdot OH.$$

* They will probably be shown to be ethereal alcohol derivatives, for several compounds, closely resembling glucosides in behaviour, have been synthesised by dissolving sugars in alcohols and saturating with hydrogen chloride. In this way, methyl alcohol and glucose have yielded *methylglucoside*, $C_6H_{11}(OCH_3)O_5$.

Arbutin, $C_{12}H_{16}O_7$, is found in the leaves of the bear-berry (*Arbutus uva ursi*), an astringent plant of the Heath order, sometimes used medicinally, and in *Pyrola umbellata*, also a medicinal plant of the closely allied Winter-green order. It may be prepared like salicin, and crystallises in bitter needles from its aqueous solution. Emulsin or dilute acids decompose it into glucose and hydroquinone—

$$C_{12}H_{16}O_7 + H_2O = C_6H_{12}O_6 + C_6H_4(OH)_2.$$

Phlorizin, $C_{21}H_{24}O_{10}$ (φλοιός, *bark*, and ῥίζα, *root*), is extracted by hot alcohol from the root-bark of the apple, pear, plum, and cherry tree. It crystallises from hot water in bitter needles with 2Aq. When boiled with dilute acids, it yields glucose and *phloretin*; $C_{21}H_{24}O_{10} + H_2O = C_6H_{12}O_6 + C_{15}H_{14}O_5$. When exposed to air in the presence of ammonia, it is converted into a fine purple colouring-matter, *phlorizein*, $C_{21}H_{30}N_2O_{13} = (C_{21}H_{24}O_{10} + 2NH_3 + O_3)$. It melts at 108° C.

Glycyphyllin, $C_{21}H_{24}O_9$, is a crystalline substance allied to phlorizin, extracted from the leaves of *Smilax glycyphylla*, an Australian plant of the Sarsaparilla order. It is sparingly soluble in cold water, but dissolves in hot water and in alcohol. Its solution tastes like liquorice. It does not reduce alkaline copper solutions, and is not precipitated by normal lead acetate, though it is by the basic acetate. When boiled with dilute sulphuric acid, it yields phloretin and rhamnose (p. 725)—

$$C_{21}H_{24}O_9 + H_2O = C_{15}H_{14}O_5 + C_5H_9(CH_3)O_5.$$

Hesperidin, $C_{22}H_{26}O_{12}$, is contained in the fruit, leaves, and stalks of the orange-tree and other members of the same family; it is resolved by acids into glucose and *hesperitin*, $C_{16}H_{14}O_6$.

Æsculin, $C_{15}H_{16}O_9$, is extracted by boiling water from the bark of the horse-chestnut (*Æsculus hippocastanum*), sometimes used as a febrifuge. The infusion of the bark is mixed with lead acetate, to precipitate the tannin and colouring-matter, filtered, the excess of lead precipitated by H_2S, and the filtered solution evaporated, when æsculin crystallises in colourless needles containing ½Aq. sparingly soluble in cold water, but readily in hot water and in alcohol. The aqueous solution is slightly bitter, and has a strong blue fluorescence, destroyed by acids and restored by alkalies. Emulsin and boiling dilute acids convert æsculin into glucose and *æsculetin*, a dihydroxycoumarin (p. 611)—

$$C_{15}H_{16}O_9 + H_2O = C_6H_{12}O_6 + C_9H_6O_4.$$

Æsculetin exists, in small quantity, in horse-chestnut bark. *Paviin* or *fraxin*, $C_{16}H_{18}O_{10}$, accompanies æsculin in horse-chestnut bark. It is more soluble in ether than is æsculin, and has a green fluorescence. Fraxin is obtained in larger quantity from the bark of the ash (*Fraxinus excelsior*), which is also febrifugal. Trees of the genus *Pavia*, belonging to the same order as horse-chestnut (*soap-worts*), yield more paviin than æsculin.

548. **Amygdalin**, $C_{20}H_{27}NO_{11}$, is extracted from bitter almonds, the kernels of the fruit of *Amygdalus communis*, of which one variety yields the sweeet almond, containing no amygdalin. The almonds are pressed to extract the fixed oil (not the *essential oil*, but a glyceride), and the *bitter-almond cake* is boiled with alcohol, from which the amygdalin crystallises in pearly scales which dissolve in water, and crystallise from it in prisms with 3Aq. Amygdalin may also be extracted from the kernels of peaches and nectarines, both fruits of varieties of amygdalus. It is also present in the leaves and kernels of several species of cherry, and the bitter-almond oil formed from it confers the flavour upon cherry-brandy, noyau, ratafia, and maraschino. The production of glucose, hydrocyanic acid, and benzoic aldehyde, by the action of emulsin on solution of amygdalin, has been already noticed (p. 584). When long boiled with baryta, it yields ammonia and the barium salt of *amygdalic acid*, $C_{20}H_{28}O_{13}$. This acid is a glucoside, for when boiled with dilute acids it is converted into glucose and *mandelic acid* (p. 609)—

$$C_{20}H_{28}O_{13} + 2H_2O = 2C_6H_{12}O_6 + C_8H_8O_3.$$

Daphnin, $C_{15}H_{16}O_9$, isomeric with æsculin, is obtained from the bark of *Daphne mezereum*, used as a remedy for toothache. Dilute acids convert it into glucose and *daphnetin*, a dihydroxy-coumarin (p. 591); $C_{15}H_{16}O_9 + H_2O = C_6H_{12}O_6 + C_9H_6O_4$.

Convolvulin, $C_{31}H_{50}O_{16}$, and its homologue *jalapin*, $C_{34}H_{56}O_{16}$, are the purgative principles of certain of the *Convolvulaceæ*, such as *jalap* and *scammony*. They are amorphous bodies, which yield glucose, and, respectively, *convolvulinol*, $C_{13}H_{24}O_3$, and *jalapinol*, $C_{16}H_{30}O_3$, when hydrolysed by acids or emulsin. *Turpethin*, isomeric with jalapin, is extracted from the roots of *Convolvulus turpethum*, also used as a purgative.

Helleborein, $C_{26}H_{44}O_{15}$, is the narcotic poison from the root of *black hellebore*, a plant of the Buttercup order. It crystallises in needles, which dissolve easily in water, but sparingly in alcohol.

Digitalin is the poisonous glucoside extracted from the seeds of the foxglove (*Digitalis purpurea*). It is crystalline, sparingly soluble in water and ether, but dissolves in alcohol and chloroform. Strong sulphuric and hydrochloric acids dissolve it with a green colour. Its formula is not known.

Saponin, $C_{32}H_{54}O_{18}$, is found in the soap-wort, in the root of the clove-pink, which belongs to the same natural order (*Caryophyllaceæ*), in the pimpernel, and in the fruit of the horse-chestnut. It may be extracted by boiling alcohol, which deposits it as an amorphous powder on cooling. It is soluble in water, and its solution lathers like soap. This leads to the use of decoctions containing it, such as that of the soap-nut of India, for cleansing delicate fabrics. The dry powder of saponin causes sneezing.

Coniferin, $C_{16}H_{22}O_8.2Aq$, crystallises from the gummy liquid found, in the spring, between the inner and outer barks of coniferous trees. In contact with water and emulsin, it yields glucose and *coniferyl alcohol*—

$$C_{16}H_{22}O_8 + H_2O = C_6H_{12}O_6 + C_{10}H_{12}O_3.$$

The latter is a crystalline body, soluble in ether, and smelling of vanilla. When distilled with potassium dichromate and sulphuric acid, it yields acetic aldehyde and *vanillin*; $C_{10}H_{12}O_3 + O = C_2H_4O + C_8H_8O_3$ (p. 586).

Quercitrin, $C_{21}H_{22}O_{12}$, is the colouring-matter of quercitron bark, and is also found in horse-chestnut flowers, and in grape-vine, sumach and catechu. It may be extracted from quercitron bark by alcohol, the tannin precipitated by solution of gelatine, and the filtrate evaporated. Quercitrin forms yellow crystals, sparingly soluble in water. Dilute sulphuric acid converts it into *rhamnose* and *quercetin*; $C_{36}H_{38}O_{20} + H_2O = 2C_5H_9(CH_3)O_5 + C_{24}H_{16}O_{11}$. This last, also called *flavin*, is found in heather, in tea, and in the root bark of apple and other trees. It is a yellow crystalline body, which is sparingly soluble in water and more soluble in alcohol. It may be sublimed in yellow needles. *Rutin*, which occurs in rue and in capers, much resembles quercitrin.

Antiarin, $C_{14}H_{20}O_5.2Aq$, is the principle of the Javanese arrow-poison, *upas-antiar*, the juice of *Antiaris toxicaria*, a large tree of the Bread-fruit tribe. It may be crystallised from the alcoholic extract of upas, and is soluble in water and ether. With acids, it behaves like a glucoside.

549. **Bitter Principles.**—*Picrotoxin*, $C_{30}H_{34}O_{13}$, is a narcotic poison contained in *Cocculus indicus*, the fruit of *Anamirta paniculata*, a tropical trailing shrub of the order *Menispermaceæ*. The fruit has been sometimes used as a *hop-substitute* by brewers. Picrotoxin may be extracted from the seeds by boiling with alcohol, from which it crystallises in needles; it is sparingly soluble in water, and soluble in ether; it is a mixture of *picrotoxinin*, $C_{15}H_{16}O_6 + H_2O$, and *picrotin*, $C_{15}H_8O_7$. *Quassiin*, $C_{22}H_{40}O_{10}$, is another crystalline bitter principle, extracted by alcohol from *quassia* chips, the wood of *Picrasma excelsa* (bitterwood). This is also said to be used as a hop-substitute, and is not poisonous, except to flies. It is administered as a tonic. Water dissolves it sparingly, but acquires a bitter taste. *Calumbin*, $C_{21}H_{22}O_7$, is a substance of the same kind, extracted from *calumba root* (*Cocculus palmatus*).

Santonin, $C_{15}H_{18}O_3$, is the bitter principle of the seeds of *Artemisia santonica* (*worm-seed*) and of *Artemisia absinthium* (*wormwood*); it may be extracted from absinthium by mixing it with lime and boiling with weak alcohol; the solution is evaporated and the residue boiled with acetic acid, which deposits colourless prisms of santonin, which become yellow when exposed to light. It is insoluble in water, but dissolves in alcohol and ether; it is dissolved by alkalies, yielding santonates, *e.g.*, *sodium santonate*, $NaC_{15}H_{19}O_4$, from which *santonic acid*, $HC_{15}H_{19}O_4$, may be obtained by shaking with HCl and ether; thus it appears to be a lactone. It contains a ketonic group. Santonin is moderately poisonous, and affects the perception of colours, rendering violet invisible; it is contained in the liqueur known as *crême d'absinthe*, or *Wermuth*. *Gentianin*, $C_{14}H_{10}O_5$, is extracted by ether

from the roots of the yellow gentian, used as a bitter and tonic. It forms yellow needles, sparingly soluble in water, but freely in alcohol and ether; also soluble in alkalies, with a strong yellow colour.

Elaterin (ἐλατήριος, driving away, in allusion to its drastic quality), $C_{20}H_{28}O_5$, is the active principle of the drug *elaterium*, obtained from the juice of the squirting cucumber (*Momordica elaterium*). It is crystalline, insoluble in water, but soluble in alcohol and ether. It admits of sublimation. *Kosine*, $C_{31}H_{38}O_{10}$, is the active principle of *Kousso*, an Abyssinian plant used as a vermifuge; it crystallises in yellow needles, which are insoluble in water, but soluble in ether and alcohol. *Aloin*, $C_{17}H_{18}O_7$, is a crystalline bitter-sweet substance extracted from *aloes*, the dried juice of various species of aloe.

Glycyrrhizic acid (formerly called *glycyrrhizin*), $C_{44}H_{63}NO_{19}$, is extracted from dried *liquorice root* (*Glycyrrhiza glabra*) by dilute acetic acid; alcohol is added and the filtrate evaporated to a syrup. It is amorphous and has a sweet taste.

Cantharidin, $C_{10}H_{12}O_4$, is extracted from the Spanish fly and other insects. It is a bitter substance, melting at 218° C. and subliming. It blisters the skin.

550. **Vegetable Colouring-Matters.**—Notwithstanding the great variety and beauty of the tints exhibited by plants, comparatively few yield colouring-matters which are sufficiently permanent to be employed in the arts, the greater number of them fading rapidly as soon as the plant dies, since they are unable to resist the decomposing action of light, oxygen, and moisture, unless supported by the vital influence in the plant; some of them even fade during the life of the plant, as may be seen in some roses which are only fully coloured in those parts which have been screened from the light. Diligent research has disclosed the constitution of many of the vegetable colouring-matters, such as those of the madder and indigo plants; these are considered under the classes of compounds to which they belong. Those which are described here are still under investigation, and little is yet known of their chemistry save that many are glucosides.

Chlorophyll (from χλωρός, *green*; φύλλον, *a leaf*), the abundant green colour of plants, has not been obtained in a pure state, because it neither crystallises nor volatilises. The want of exact knowledge of the chemistry of this body is especially felt, because its physiological importance to plants is of the highest order. It is evidently active in constructing the tissues of the plant from carbonic acid, water, ammonia, &c., derived from the air and soil. It may be extracted from the leaves of plants by boiling with alcohol, ether, or benzene.

The alcoholic extract of the leaves is allowed to stand for some time, then filtered and shaken with one volume of ether and two volumes of water. The ethereal layer, which contains all the chlorophyll, is shaken with water as long as the latter reduces Fehling's solution; it is then allowed to evaporate, the chlorophyll remaining as a bright green residue. When this is dissolved in alcohol, and boiled with dilute H_2SO_4 or HCl, the solution gives the glucose reaction with Fehling's solution, rendering it probable that chlorophyll is a glucoside. Chlorophyll dissolves, in cold strong sulphuric acid, to a green solution which gives a dark green precipitate on dilution, and the filtrate gives the glucose reaction.

An alcoholic solution of chlorophyll is very unstable in air, especially when exposed to light, but gives rise to two stable colouring-matters, *phylloxanthin* and *phyllocyanin* when treated with acids; the precipitate obtained is dissolved in ether and the solution is shaken with strong HCl, which dissolves the phyllocyanin and settles as a bright blue layer below the ethereal solution of the phylloxanthin, which is yellowish-green. The phyllocyanin yields a remarkably stable bright green colouring-matter with copper, the production of which is probably the

cause of the improved colour of preserved vegetables which have been treated with a small dose of a copper salt.

When distilled with zinc-dust chlorophyll yields pyrrol, and the same result has been obtained with the colouring-matter of the blood; thus these two substances, so mysteriously essential to life, appear to be offspring of the same chemical parent.

Iron is said to be an essential constituent of chlorophyll; if iron be absent from the plant's food, chlorophyll is not developed.

The blue colouring-matter contained in many flowers, such as the violet, has been named *cyanin*. Acids redden it, and hence only those flowers which have a neutral juice are blue; red flowers yielding an acid juice. The colouring-matter of grapes and of red wine appears to be cyanin.

551. **Saffron** is a yellow colouring-matter, obtained from the flowers of *Crocus sativus*, which are purple, with yellow anthers. When these are dried and pressed into cakes they form the saffron of commerce, which has an agreeable odour. It is chiefly imported from Spain, and is often adulterated. It gives up to water and alcohol a yellow amorphous glucoside, termed *polychroite*. *Annatto*, or arnotto, is another yellow colouring-matter, which forms the pulp round the seeds of *Bixa orellana*, a West Indian shrub. It is used for colouring butter and cheese. The colouring principle has been called *bixin;* it is sparingly soluble in water, but dissolves in alcohol and in alkalies; acids reprecipitate it without much change of colour.

Turmeric is the root of an East Indian plant, the *Curcuma longa*, and is used in curry. It contains a crystalline yellow body, *curcumin*, $C_{21}H_{20}O_6$, which may be extracted by boiling benzene. It is insoluble in water, but dissolves in alcohol with a green fluorescence. Alkalies dissolve it, forming red salts, from which acids precipitate it of a yellow colour. Paper dyed with turmeric is used as a delicate test for alkalies, which turn it brown. When acted on by boric acid and strong sulphuric acid, it is converted into *rosocyanin*, which crystallises in green needles dissolved by alcohol, with a red colour, which is changed to deep blue by alkalies. Turmeric-paper is used in testing for boric acid (p. 274).

Weld is the *Reseda luteola*, a plant of the Mignonette order, the leaves of which give a yellow solution when boiled with water. The hot decoction, mixed with alum and chalk, gives a yellow precipitate, which is used in paper-staining. It contains a crystalline yellow body, *luteolin*, $C_{15}H_{10}O_6$, sparingly soluble in water, but dissolved by alcohol and by alkalies. It sublimes in yellow needles.

Fustic is a yellow dyestuff, of which there are two kinds. *Old fustic* is the wood of a tree of the Mulberry order (*Morus*, or *Maclura tinctoria*), grown in the West Indies. *Young fustic* is the wood of *Rhus cotinus*, or Venice sumach, from Italy and the South of France. When old fustic is boiled with water, the solution deposits yellow needles of *morin*, $C_{13}H_8O_6$, soluble in alcohol. The mother-liquor of morin, when evaporated, yields *maclurin* or moritannic acid (p. 611).

Gamboge is a yellow gum-resin, originally obtained from Camboja in Asia, and is exuded by certain species of Guttiferæ. It contains about 30 per cent. of a yellow gum, soluble in water, and 70 per cent. of resin soluble in alcohol and alkalies, called *gambodic acid.*

Purrée (*púrî*), or *Indian yellow*, imported from India and China, and said to be the dried excrement of buffaloes fed on mango leaves, is a compound of magnesia with *euxanthin* (or *euxanthic acid*), $C_{19}H_{16}O_{10}$. By extracting it with hydrochloric acid and alcohol, the euxanthin is obtained in yellow prisms, sparingly soluble in water, soluble in alcohol, ether, and alkalies. When heated, it yields a yellow crystalline sublimate of *euxanthone*, $C_{13}H_8O_4$. On fusion with potash, euxanthone yields hydroquinone, and nitric acid converts it into trinitroresorcin, which oppose the idea that purrée is of animal origin.

552. **Safflower**, which yields *rouge*, consists of the dried flowers of *Carthamus tinctorius*, cultivated in Egypt. It contains a yellow substance, which may be extracted by water, and a red colour, *carthamin*, $C_{14}H_{16}O_7$, which may be dissolved out by sodium carbonate, and precipitated by acetic acid. Alcohol dissolves it to a red solution. It is used in dyeing, but soon fades when exposed to light.

Carotin, $C_{18}H_{24}O$, is a red substance, found in small crystals in the cells of the carrot. It crystallises from alcohol in cubes of agreeable odour.

Santalin, $C_{15}H_4O_5$, is the colouring-matter of *red sanders wood* (*Pterocarpus santalinus*), from which it may be extracted by alcohol, which deposits it in red crystals insoluble in water, but giving violet solutions with alkalies.

Hæmatoxylin, $C_{16}H_{14}O_6.3H_2O$, is extracted from *logwood* (*Hæmatoxylon campechianum*), which grows at Campeachy in the Bay of Honduras, by boiling the chips with water. It is deposited from the solution in yellow needles, which are soluble in water, alcohol and ether. It resembles the phenols by dissolving in alkalies to a purple solution, which absorbs oxygen and forms a red colouring-matter, *hæmatein*, $C_{16}H_{12}O_6$, sparingly soluble in cold water, which may also be obtained by oxidising hæmatoxylin, in ethereal solution, with nitric acid. Reducing-agents, such as sulphurous acid, convert it into hæmatoxylin. When fused with potash, hæmatoxylin yields pyrogallol. It contains five OH groups.

Potassium chromate gives an intense black colour with infusion of logwood, which has been used as an ink, but is fugitive. Logwood boiled with distilled water gives a yellow solution, but with common water it gives a fine purple-red, from the production of hæmatein by the oxidation of the hæmatoxylin in presence of the calcium carbonate in the water. The solution of logwood is sometimes used as an *indicator* in alkalimetry.

Brazilin, $C_{16}H_{14}O_5$, is contained in Brazil wood (*Cæsalpinica brasiliensis*); peachwood (*C. echinata*), and Sappan wood (*C. sappan*)—all dyewoods from the same botanical sub-order as logwood. Brazilin, when quite pure, forms colourless crystals, and yields colourless solutions in air-free water and alcohol; but it soon becomes yellow by oxidation, and dissolves in alkalies with a fine red colour, which is bleached by reducing-agents. It contains four OH groups.

553. **Lac** is a red dye extracted from the resinous exudation of certain tropical trees of the Fig tribe, punctured by an insect (*Coccus*). In its crude, natural state, encrusting the small branches, it is known as *stick-lac*, and has a deep red colour; when broken off the branches and boiled with water containing sodium carbonate, it gives a red solution, from which the colouring-matter is precipitated as a *lake* by adding alum, and made into cubical cakes for the market. The resinous matter (about 68 per cent.) left undissolved by sodium carbonate, is termed *seed-lac*; this is melted, strained through a cloth, and allowed to solidify in thin layers, when it forms *shell-lac*, which is much used in the manufacture of sealing-wax and varnishes. The *lacquer* applied to brass is named after this resin, being an alcoholic solution of shell-lac, sandarach, and Venice turpentine. *Indian ink* is made by mixing lamp-black with a solution of 100 grains of lac in 20 grains of borax and 4 ounces of water.

Carmine owes its colour to *carminic acid*, $C_{22}H_{22}O_{13}$, a glucoside extracted by boiling water from the cochineal insect, which is found upon a species of cactus in Mexico and Peru. *Carmine-lake* is precipitated by alum and potassium carbonate from the aqueous extract of the cochineal insect. The acid itself is an amorphous purple solid, easily soluble in water and alcohol, and sparingly in ether. It dissolves unchanged in strong sulphuric acid.

XV. ALBUMINOID COMPOUNDS.

554. Under this head are classed several nitrogenous products of animal and vegetable life, which are not crystalline or volatile. They resemble each other very closely in composition, containing from 50 to 55 per cent. carbon, 21 to 25.5 oxygen, 15 to 18 nitrogen, 6.7 to 7.3 hydrogen, and 0.4 to 1.7 sulphur. If the sulphur be regarded as essential to the formula, the mean of these numbers would give, approximately, the formula $C_{131}H_{210}N_{35}O_{44}S$. Concerning the constitution of these compounds very little is known. They are generally lævo-rotatory.

It has become customary among physiologists to distinguish between *proteids** and *albuminoids*. The former term is applied to such compounds as resemble albumin, or white of egg, in properties, whilst the albuminoids are typified by gelatine. The two classes of compounds differ mainly in the fact that the

* A name originally given to compounds supposed to be derived from a primary source, *protein* (πρωτεῖον, *pre-eminence*).

majority of the proteids are coagulated by heat. In what follows, only a few of the more important proteids and albuminoids will be described, since it is not possible in a general text-book to enter into details of the modern classification of these compounds.

Albumin, or *white of egg*, $C_{72}H_{112}N_{18}O_{22}S$,* may be extracted from its aqueous solution contained in the egg, by stirring it briskly to break up the membrane, adding a little acetic acid to neutralise the soda present in the white, filtering, placing for twelve hours on a dialyser (p. 278) to separate the sodium chloride and acetate, evaporating the contents of the dialyser below 50° C., powdering the residue, and treating with ether to extract fatty matters. The albumin so prepared is an amorphous solid, of sp. gr. 1.31.† When heated, it swells up, carbonises, and evolves offensive alkaline vapours, usually leaving a slight alkaline ash, containing a trace of calcium phosphate, which is very difficult to separate completely from the albuminoids.

In cold water, albumin slowly softens and dissolves, like gum; if this solution be heated to about 70° C., the albumin is converted into an insoluble form, becoming a white, soft solid, as in boiled eggs, if the albumin amounts to 12 per cent., and a flocculent precipitate if the solution be diluted. The *coagulated* albumin is not easily dissolved by acids or alkalies, and is believed to be the anhydride of soluble albumin, for if it be heated in water in a sealed tube to above 150° C., it is dissolved to a reddish liquid, which behaves like a solution of ordinary albumin, but is not coagulated by heat. Raw white of egg is inodorous, and does not blacken silver; but after boiling it smells of H_2S, and blackens silver, showing that it suffers some decomposition during coagulation. When dried, coagulated albumin forms a translucent brittle mass, which becomes white and opaque in water. Soluble albumin, completely dried below 50° C., may afterwards be heated to 100° C., without becoming insoluble.

Alcohol precipitates albumin from its solution, and the soluble is converted into the insoluble form by digestion with strong alcohol. It is also precipitated by shaking with ether or turpentine.

In many reactions albumin resembles the amido-compounds, as in playing the part of a weak acid and a weak base. Strong potash added to a solution of albumin precipitates a gelatinous compound of potash and albumin, which is soluble in boiling water, and gives, with metallic salts, precipitates containing albumin and metallic oxides. Acids coagulate the solution of potash-albumin.

The mineral acids, except ortho- and pyro-phosphoric acids, precipitate a solution of albumin, the precipitate being a compound of the acid with albumin, but the organic acids, except picric, do not, as a rule, precipitate it. Many of the compounds of albumin and acid have been proved to have a definite composition. Nitric acid has long been employed as a test for albumin (in urine, for example), since it forms a precipitate even in a very weak solution, but if the liquid be mixed with a very minute quantity of the acid, the flocculent precipitate formed at first disappears on shaking, and the clear acid liquid is not precipitated by boiling. The same thing is observed with sulphuric and hydrochloric acids.

To obtain definite compounds of albumin with the acids, beaten white of egg is placed in a dialyser suspended upon the surface of the very diluted acid for about 24 hours, when the acid passes through the dialyser and combines with the albumin. The products are nearly colourless jellies soluble in hot water.

The reagents commonly employed for precipitating albumin are nitric acid,

* The simplest formula for crystallised albumin is said to be $C_{720}H_{1124}N_{216}S_3O_{242}$.

† It is stated that by adding a saturated solution of ammonium sulphate to egg albumin, filtering and evaporating the filtrate, crystals of albumin may be obtained.

mercuric chloride, potassium ferrocyanide, and picric acid. Of these, nitric and picric acids precipitate all the above compounds of albumin with the acids: potassium ferrocyanide precipitates all except the metaphosphate, citrate, and oxalate; mercuric chloride only precipitates the hydrochloride and the metaphosphate.

Strong hydrochloric acid gives with albumin a precipitate which dissolves in excess, and gives a purplish solution when boiled in contact with air. Strong nitric acid colours coagulated albumin yellow; alkalies dissolve the yellow mass to an orange liquid, from which acids precipitate yellow flakes (*xantho-proteic acid*). Albumin also gives a fine red colour with mercuric nitrate containing nitrous acid (*Millon's test;* prepared by dissolving mercury in twice its weight of nitric acid, in the cold, and adding twice its bulk of water). When boiled with moderately dilute sulphuric acid, albumin yields leucine and tyrosine (p. 678). With solution of potash, on boiling, it also gives leucine and tyrosine, evolves one-third of its nitrogen as ammonia, and its sulphur is converted into potassium sulphide, which gives a black precipitate on adding a salt of lead. When heated with baryta-water to 150° C., it evolves part of its nitrogen as ammonia, and barium carbonate is formed in the same ratio to the ammonia as when urea is heated with baryta; this has led to the conclusion that albumin contains one-fifth of its nitrogen in a form nearly allied to urea, and that it is probably a complex ureide (p. 671). When oxidised by potassium permanganate, it yields benzoic acid. Boiled with a mixture of potassium permanganate and potash, it evolves the whole of its nitrogen as ammonia, whilst with potash alone it only gives off one-third of its nitrogen.

The putrefaction of the albuminoids gives rise to the *ptomaines* or *toxines*; p. 666. Such poisonous products are also formed by the bacilli of diseases like diphtheria, and it is upon the introduction into the system of antidotes (*anti-toxines*), derived from animals that have been able to survive the poisons, that the principle of inoculation depends.

555. The gastric juice dissolves coagulated albumin digested with it at about 37° C., and the solution is not precipitated by potassium ferrocyanide, nor coagulated by heating. In this condition it is said to have been *peptonised*, or converted into *peptone* (*πέπτω*, to *digest*). The constituent of the gastric juice which effects this change is termed *pepsin*, and may be precipitated from the juice by alcohol. It resembles albumin in composition, but is much less putrescible. When dissolved in dilute hydrochloric acid, also present in the gastric juice, it yields a mixture which peptonises most albuminoids if digested at about 40° C. The pepsin prepared from the stomach of the pig and other animals is sometimes administered medicinally to assist digestion.

The action of pepsin and HCl on albuminoids is hydrolytic and occurs in several stages, the successive products between the original compound and peptone being a *syntonin* or *acid-albumin* and an *albumose* or *propeptone*.

Serum albumin forms nearly 8 per cent. of the serum of blood, and is found in other liquid secretions. It may be prepared by precipitating the diluted serum with lead acetate, suspending the washed precipitate in water, and decomposing it with CO_2; the filtered liquid is then evaporated below 50° C. It appears to contain less sulphur than ovalbumin (egg albumin) in the ratio of 1.2 : 1.6, but rather more oxygen (23.1 : 22.4). In properties it very closely resembles ovalbumin, but it is not coagulated by ether, and gives precipitates with nitric and hydrochloric acids, which are more easily dissolved by excess than are those of egg albumin. It is more powerfully lævo-rotatory than egg albumin.

Vegetable albumin is the substance which is precipitated by heat from the juices of plants, and from their infusions in cold water. It has not been obtained pure in the soluble condition. It appears to contain less sulphur even than serum albumin contains.

Globulin, or *serum globulin*, is very like albumin, but is insoluble in pure water: it dissolves in a very weak solution of salt, and in very weak acids and alkalies. It dissolves in water saturated with oxygen, and is precipitated by carbon dioxide. This gas precipitates it in a granular form from the serum of blood; saturation of

the serum with salt also precipitates it. *Crystallin* is found in the aqueous humour and crystalline lens of the eye.

Myosin (*μῦς*, a muscle) separates from *muscle plasma* (the liquid contained in living muscle) after death, producing *rigor mortis*. Chopped flesh is triturated to a pulp with common salt, 9 parts of water are added for 1 of salt, the whole digested for some time at 24° C., pressed through linen and filtered; the myosin is precipitated on adding much water or salt.

556. **Fibrin** is the albuminoid which separates from the blood when this has been shed from the animal, causing the coagulation or clotting of the blood plasma. It appears to be formed from *fibrinogen*—a soluble albuminoid existing in the plasma—by a ferment (*thrombin*) contained in the white blood corpuscles. Human blood yields about 0.25 per cent. of fibrin, which resembles myosin, but is not dissolved by solution of salt. It may be obtained from freshly drawn blood by whipping it with a bunch of twigs, when the fibrin adheres to them in threads which become nearly white when washed, and may be freed from fat by alcohol and ether. If the blood be not stirred when freshly drawn, it forms a red *clot*, caused by the coagulation of the fibrin, and the entanglement in it of the red blood corpuscles; if the clot be cut up and washed in a cloth, the corpuscles and *blood serum* may be washed away and the fibrin left. If 7 measures of blood be drawn into a vessel containing 1 measure of a cold saturated solution of Na_2SO_4, the fibrin will remain in solution, whilst the blood-globules will be deposited on standing. The clear yellow solution containing albumin, globulin, and fibrinogen is largely diluted with water, when fibrin is precipitated.

Fibrin forms elastic strings which dry into a yellow horny mass. When fresh, it readily absorbs oxygen, and evolves CO_2; when moist it decomposes H_2O_2, evolving O. It is insoluble in water, alcohol, solution of salt, and in cold very dilute HCl (0.1 per cent.), but this dissolves it at 60° C. Solution of nitre at 40° C. also dissolves it. When heated for some time with water at 72° C., it becomes insoluble in dilute acids and salts, but dissolves in alkalies. Boiled for many hours with water, one-fifth of it may be dissolved, yielding a solution having some of the properties of gelatine. Heated with water at 120° C. for some hours, it is almost entirely dissolved. The solution of fibrin in weak HCl is precipitated by neutralisation and by saline solutions. The precipitate always contains a little calcium phosphate. Fibrin soaked in weak potash becomes gelatinous and, if heated to 60° C., dissolves to a solution resembling that of albumin. Fibrin is hardened and rendered non-putrescible when soaked in solution of tannin. Moist fibrin soon begins to putrefy when exposed to air, and becomes fluid in a week; the products of putrefaction resemble those from albumin.

Fibrinogen may be precipitated from blood plasma by a solution of salt which is semi-saturated, and can in this way be separated from the serum globulin.

Fibrin from blood contains more nitrogen than the albumin of serum (17.4 : 15.6) and a little less oxygen (21.8 : 23.1). It does not appear that blood-fibrin and flesh-fibrin are identical.

557. **Casein** is the chief constituent of the curd of milk, and differs from the other albuminoids in not coagulating spontaneously or on heating. It exists in milk as a soluble compound with a little potash or soda, and is separated as curd when the alkali is neutralised either by adding an acid, or by the formation of acid (lactic) by the decomposition of milk-sugar caused by spontaneous fermentation.

It is prepared by precipitating diluted milk with acetic acid and washing the precipitate with water, alcohol, and ether in succession, to remove soluble matters and fat; it is further purified by dissolving in weak soda and precipitating it by acetic acid. Coagulated casein is characterised by the facility with which it is dissolved by weak alkaline solutions, yielding a liquid upon the surface of which, when boiled, an insoluble pellicle forms, like that produced on the surface of boiled

milk. Coagulated casein may also be dissolved by acetic or oxalic acid, but sulphuric or hydrochloric acid reprecipitates it, these acids forming compounds with casein which are insoluble in the acids, but soluble in water. If skimmed milk be carefully evaporated to dryness, and the fat extracted from the residue by ether, the casein is left in the soluble form mixed with milk-sugar, and may be dissolved in water or in dilute alcohol.

A distinctive property of casein is its coagulation by *rennet*, the mucous membrane of the stomach of the calf, a small quantity of which or of its solution in brine,* coagulates the casein in a large quantity of milk; the coagulation does not appear to depend upon the formation of lactic acid, but upon a specific action of the rennet; the curd thus produced contains calcium and magnesium phosphates, and is not easily soluble in sodium carbonate. The casein of milk is more readily coagulated by acids and by rennet when the milk is warmed; hence milk which has undergone very slight fermentation is curdled when heated, but if fresh milk be heated to boiling, the decomposition will be prevented. The casein of milk is precipitated by some neutral salts, such as sodium chloride or magnesium sulphate, and even by an excess of sodium carbonate.

At the present time, the condition in which casein exists in milk and the cause of its coagulation by rennet are subjects of much discussion. Some chemists claim that the milk contains *caseinogen*, which is precipitated by acids, and differs from casein into which it is converted by rennet. According to Hammarsten, caseinogen is only coagulated by rennet when it contains earthy phosphates, which combine with the casein produced and precipitate it. A solution of casein free from lime salts is not precipitated by rennet, but the precipitation occurs on adding a lime salt, even though the rennet has been made inactive by heating the casein solution containing it.

The general chemical behaviour of casein resembles that of albumin. It contains a little less sulphur than albumin and fibrin contain, and phosphorus appears to be an essential constituent (0.85 per cent.).

Casein combines with slaked lime to form a hard insoluble mass, so that a mixture of cheese with lime is sometimes used as a cement for earthenware. The curd of milk, washed and dried, is used by calico-printers, under the name of *lactarine*, for fixing colours. If it be dissolved in weak ammonia, mixed with one of the aniline dyes, printed on calico, and steamed, the colour is left as an insoluble compound with the casein. By treating coagulated casein with formaldehyde it becomes similar to horn, for which it is substituted in making combs and the like.

Legumin, or *vegetable casein*, is found in peas, beans, and most leguminous seeds. If dried peas be crushed and digested for some time in warm water, a turbid liquid is obtained, holding starch in suspension; this is allowed to settle, the supernatant liquid precipitated by acetic acid, and the legumin purified from fat by washing with alcohol and ether. It closely resembles casein, its solution forming a pellicle when heated, and being coagulated by rennet. In composition it differs somewhat from casein, containing about 1 per cent. more nitrogen, and only about half as much sulphur. When boiled with dilute sulphuric acid, legumin yields much less leucine than albumin and fibrin furnish, and very little tyrosine: but it gives more aspartic acid and *glutamic acid*, $C_3H_5(NH_2)(CO_2H)_2$, homologous with aspartic acid.

Gluten is the tough, sticky substance which is left when flour is made into dough, tied up in muslin, and kneaded in water as long as any starch passes through. It speedily putrefies when exposed to the air, and dries up to a brittle, horny mass at 100° C. When fresh gluten is boiled with dilute alcohol, a portion is left undissolved, and has been named *vegetable fibrin*, as it forms a tough elastic mass. It dissolves in very dilute HCl and in dilute alkalies, and is precipitated by acetic acid and by salts. When the alcoholic solution cools, it deposits white flakes of *mucedin*.

* The active principle (*lab* or *chymosin*) of the rennet may be obtained from rennet extract by saturating it with salt, when the lab will rise to the surface.

and on adding water to the filtrate, *gliadin* is precipitated. These substances resemble legumin in composition, but contain twice as much sulphur.

It has been asserted that gluten does not exist, as such in flour, but is produced from the proteids in the flour by the action of water, which may enable a ferment to effect the conversion.

558. **Gelatine.**—This substance is so called from *gelu, ice*, because its solution in hot water becomes a transparent jelly on cooling. It contains 50 per cent. C, 25.7 O, 17.7 N, and 6.6 H, numbers which approximate to $C_{42}H_{66}N_{13}O_{16}$, but its molecular formula has not been determined, because it cannot be converted into vapour, and does not form well-defined compounds with other bodies. It may be obtained by digesting bones in cold dilute hydrochloric acid, till the calcium phosphate and other salts are dissolved, leaving a residue of the same form as the bone, but of a soft, flexible character. This is termed *osséin*, and has the same composition as gelatine, into which it is converted by long boiling with water, especially under pressure, a solution being obtained which becomes a jelly on cooling, and leaves a brittle, transparent mass (*glue*) when dried. Gelatine does not fuse when heated, but swells up and decomposes, yielding very offensive alkaline vapours, containing ammonia and compound ammonias (methylamine, &c.), pyrrol, and its derivatives, toluene, naphthalene, ammonium cyanide, water, &c. *Dippel's oil*, obtained by distilling bones, contains these products, together with others, in the formation of which the fat of the bones takes part, such as the cyanides of the fatty acid series (propionitrile, &c.), pyridine bases, phenol, and aniline.

Gelatine softens and swells in cold water, but does not dissolve; hot water dissolves it, and the solution gelatinises on cooling, even when it contains only 1 per cent. Continued boiling of the solution destroys the tendency to gelatinise. Gelatine is insoluble in alcohol, which precipitates it in white flakes from its aqueous solution. It is also precipitated by tannin, which combines with it to form an insoluble non-putrescible compound. Mercuric chloride also precipitates solution of gelatine. If gelatine solution be mixed with potassium dichromate, the jelly formed on cooling becomes insoluble on exposure to light, which is turned to account in photography; the action probably consists in an oxidation of the gelatine. Acetic acid dissolves gelatine (*liquid glue*); alkalies also dissolve it. When boiled with strong alkalies or with diluted sulphuric acid for a long time, it yields leucine and glycocine (sugar of gelatine). Heated with sulphuric acid and potassium dichromate or manganese di-oxide, gelatine yields numerous products of oxidation, among which are found many of the fatty acids, with their corresponding aldehydes and cyanides, with benzoic acid, bitter-almond oil, &c.

Gelatine may also be obtained by the action of water at a high temperature on skin, sinews, and connective tissue. *Isinglass* is very similar to gelatine and is prepared from the air-bladder of fish, especially of the sturgeon. It differs from gelatine in being liable to settle in flocks when stirred up with water; hence its application as a "fining" for beer, for which purpose it is made into an emulsion by treatment with sulphurous acid (*cutting*). *Glue* is made from the refuse and parings of hides, after being cleansed from hair and blood by steeping in lime-water, and exposed to the air for some days to convert the lime into carbonate, and prevent the injurious effect of its alkaline character upon the gelatine. They are then boiled with water till the solution gelatinises firmly on cooling, when it is run off into another vessel, kept warm to allow the impurities to settle down, after

which it is allowed to set in shallow wooden coolers. The jelly is cut up into slices and dried upon nets hung up in a free current of air. Spring and autumn are usually selected for drying glue, since the summer temperature would liquefy it, and frost would, of course, split it and render it unfit for the market. *Size* is made in a similar manner, but finer skins are employed, and the drying is omitted, the size being used in the gelatinous state. The best size is made from parchment cuttings. Moist gelatine easily putrefies, becoming very offensive: for this reason size is often treated with sulphurous acid.

Chondrin (χόνδρος, cartilage) is prepared by the action of water at a high temperature on the cartilages of the ribs and joints, and resembles gelatine in composition and properties, but contains less N and a small quantity of S. The aqueous solution of chondrin is precipitated by acetic acid, by alum, and by lead acetate, which do not precipitate gelatine. When boiled with dilute sulphuric acid, it yields leucine, but no glycocine. Boiled with hydrochloric acid, it gives a solution which reduces Fehling's solution like glucose.

Sericin, or *silk-gelatine*, $C_{15}H_{25}N_5O_8$, is the so-called *gum* extracted from silk by boiling with water; it resembles gelatine, but is precipitated by basic lead acetate, and, when boiled with sulphuric acid, yields leucine, tyrosine, and *amidoglyceric acid* (*serin*), $C_2H_3(OH)(NH_2)CO_2H$. (*Cystine*, $C_3H_7NO_2S$, found in some rare urinary calculi, appears to be a sulphur derivative of serin.)

Keratin forms the chief part of horns, claws, nails, feathers, hair, and wool, and remains when these have been treated with all ordinary solvents. It is softened by long boiling with water, and is dissolved when heated with water under pressure. It swells up and gradually becomes soluble in strong alkalies and in acetic acid, especially on boiling. It contains more sulphur than do the albuminoids. *Fibroin* from silk, and *spongin* from sponge, are similar bodies.

Chitin, $C_{14}H_{30}N_2O_{10}$, is the chief constituent of the shells of lobsters, crabs and beetles, and is left after exhausting them with water, alcohol, ether, acetic acid, and alkali. It is a white translucent substance, soluble in cold strong H_2SO_4 to a solution which yields glucose when diluted: the change appears to be a hydrolysis, $4H_2O$ being absorbed to produce *glucosamine*, $C_6H_{11}(NH_2)O_5$ (2 mols.) and acetic acid (3 mols.).

Mucin is the substance which gives the viscous character to bile, saliva, and some other animal secretions, and to the slime of the snail. To prepare it, snails are cut up, triturated with sand to a pulp, boiled with water, filtered while hot, and precipitated by excess of acetic acid; the precipitated mucin is washed with weak acetic acid as long as the washings are precipitated by tannic acid, indicating peptone. Dry mucin is unaffected even by hot water. Moist mucin swells up in a remarkable manner in water, but does not dissolve: a little acid causes it to separate in flocks which do not easily dissolve in an excess of acid. Alkalies dissolve it and acids reprecipitate it. Mucin dissolves in a strong solution of salt, and is precipitated again by water. Alcohol coagulates mucin into flocks. Acid solutions of mucin are not precipitated by potassium ferrocyanide (unlike albumin). Boiling dilute acids dissolve mucin, converting it into a substance having the properties of glucose and another which resembles albumin. The composition of mucin has not been well established: it contains the same elements as albumin, but much less nitrogen.

Nuclein is contained in the nuclei of pus-globules, in the blood globules of birds and snakes, in yolk of egg, in brain, and in milk. It stands apart from other proteids, by containing about 2 per cent. of phosphorus, in actual organic combination (and not as calcium phosphate, which so constantly accompanies the albuminoids). In extracting it, advantage is taken of its insolubility in the digestive fluids. Pus-globules are treated with warm alcohol, which removes lecithin, and afterwards with a pepsin solution made from extract of pig's stomach, and containing 1 per cent. of strong HCl. The insoluble residue consists of nuclein. Pus-globules are obtained by treating the discharge, or the bandages to which it adheres, with a mixture of 1 part of a saturated solution of sodium sulphate and 9 parts of water, when the serum remains in solution, and the pus-globules sink and may be washed by decantation; if these be digested with cold dilute HCl and afterwards shaken with a mixture of ether and water, the nuclei remain as a fine powder at the bottom. Nuclein is remarkable for its insolubility in all ordinary solvents, it appears to have an acid character, and dissolves in sodium carbonate or acetate, the solution in the latter giving precipitates with salts of zinc, copper and lead. It is of considerable importance in the chemistry

of physiology, since it appears to be the chief constituent of the cell-nucleus or cytoblast (*κύω, I hold; βλαστός, a sprout*).

559. **Brain and Nervous Substance.**—The brain and nerves contain a peculiar phosphorised fat which has been termed *lecithin*, and has the empirical formula $C_{42}H_{84}NPO_9$. It is a glycerine derivative, and its reactions show that it contains the group C_3H_5 (glyceryl), and probably the radicles of palmitic and oleic acids, and a phosphorised group, $N(CH_3)_3{\cdot}C_2H_4(PO_2)O_2$, closely related to neurine, $N(CH_3)_3{\cdot}C_2H_3{\cdot}OH$ (p. 666). A variation in the fatty acid radicles gives rise to lecithins of different formulæ, which appear to be constant constituents of the cell-material of organised bodies, both animal and vegetable, and hence necessitate a constant supply of phosphorus in the food of plants and animals.

Lecithin may be prepared from the substance of the brain by exhausting it with ether, treating the residue with alcohol, and cooling the alcoholic solution in ice, when a mixture of lecithin and cerebrin is deposited. On treating this with ether, the lecithin is dissolved, and may be purified by evaporating the ether, redissolving in alcohol, adding an alcoholic solution of platinic chloride, and decomposing the platinum salt, $(C_{42}H_{84}NPO_8HCl)_2PtCl_4$, with H_2S; on evaporating the filtrate, the lecithin is obtained as a fusible crystalline body, insoluble in water and sparingly soluble in cold alcohol and ether. It combines both with bases and acids. When boiled with acids or with potash or baryta, it yields neurine, phosphoglyceric acid, $C_3H_5(OH)_2{\cdot}PO_2(OH)_2$, palmitic and oleic acids.

Cerebrin, obtained from brain as above described, is a white powder which swells up like starch when boiled with water. It yields a substance resembling glucose when boiled with dilute acids. The formula of cerebrin, or *cerebric acid*, as it is sometimes called, appears to be $C_{17}H_{33}NO_3$. It is also found in pus-globules.

The so-called *protagon* appears to be a mixture of lecithin and cerebrin.

56c. **Hæmoglobin.**—The colouring-matter contained in the red globules of arterial blood is called *oxyhæmoglobin*, and resembles albumin in composition, except that it contains only 0.4 per cent. of sulphur and 0.43 per cent. of iron. To extract it from blood, the fibrin is separated by whipping (p. 751), and the defibrinated blood is mixed with ten volumes of a solution containing 3 per cent. of NaCl. This prevents the coagulation of the albuminoids, and the red globules subside after a day or two; the clear liquid is poured off, and the globules shaken with water and an equal volume of ether, which dissolves the envelopes of the globules, and allows the colouring-matter to pass into the water. The aqueous layer is separated, cooled in ice, one-fourth of its volume of alcohol added, and the cooling carried to $-5°$ C., when the oxyhæmoglobin crystallises in forms which vary in different animals. That obtained from the blood of men, oxen, sheep, pigs, and rabbits is not easily crystallised, the best for this purpose being the blood of dogs, guinea-pigs, hedgehogs, and rats. The crystals contain oxygen in a loosely combined form, which they evolve when exposed in a vacuum, especially if warmed, becoming thus converted into *hæmoglobin*, which again absorbs oxygen on exposure to air; this change is attended with production of a much brighter red colour, and with a difference in the action on transmitted light, for if white light be allowed to pass through the solution of oxyhæmoglobin contained in a test-tube placed before the slit of a spectroscope (p. 328), the green of the spectrum is seen to be crossed by two broad black bands, which are also seen when arterial blood is employed, whilst the solution of hæmoglobin exhibits only one band in the middle of the green, which is seen when venous blood is employed. This difference in the *absorption-spectrum* is best shown by reducing the solution of oxyhæmoglobin with a little ferrous sulphate, mixed with tartaric acid and ammonia in excess. The oxygen of oxy-

hæmoglobin is also displaced by passing hydrogen or CO_2, hæmoglobin being left, and the colour changing from red to purple.

Oxyhæmogoblin, when shaken with CO, parts with its oxygen and absorbs an equal volume of CO, its colour changing to purple; the absorption-spectrum exhibits two dark bands, which are situated further from the sodium-line (D) and nearer to the blue of the spectrum than is the case with hæmoglobin. This is turned to account in cases of poisoning by carbonic oxide. The compound of hæmoglobin and CO may be obtained in bluish-red four-sided prisms. When solution of oxyhæmoglobin is heated above 70° C., it is decomposed into albumin, which coagulates, and another red colouring-matter, termed hæmatin.

Hæmatin, $C_{34}H_{34}N_4FeO_5$, is formed when oxyhæmoglobin is decomposed by acids. If a solution of that substance, mixed with a little NaCl, is evaporated over sulphuric acid to a syrup, mixed with 15 times its volume of glacial acetic acid, and heated on a steam-bath for several hours, it yields, on cooling, flat rhombic prisms of hæmatin hydrochloride (formerly known as *hæmin*, or *blood-crystals*) of a dark, violet-red colour, and metallic lustre, containing single molecules of hæmatin and HCl. The formation of these crystals is employed for the identification of blood-stains, the suspected matter being placed on a microscope slide, a little sodium chloride added, and glacial acetic acid allowed to run under the cover-glass; on heating till bubbles appear, and cooling, the dark red hæmin crystals become visible. Hæmatin is a magnetic substance, while oxyhæmoglobin and carbonic oxide hæmoglobin are diamagnetic.

561. **Bile Constituents.**—The chief colouring-matter of the bile is *bilirubin*, $C_{16}H_{18}N_2O_3$, which is accompanied by *bilifuscin*, $C_{16}H_{20}N_2O_4$, and *biliprasin*, $C_{16}H_{22}N_2O_6$. These may be extracted from gall-stones, in which they exist in combination with calcium. The powdered calculi are boiled with alcohol and ether to extract the cholesterin, and with dilute HCl to remove the lime. After washing and drying, the residue is boiled with chloroform, which extracts bilirubin and bilifuscin: the chloroform is distilled off and the residue boiled with alcohol, which dissolves the latter. The original residue, undissolved by chloroform, contains biliprasin, which may be extracted by boiling with alcohol.

Bilirubin crystallises from chloroform in dark-red prisms, insoluble in water and alcohol, but soluble in alkaline liquids, and imparting a yellow colour to a very large volume of solution. It appears to have acid properties. Its alkaline solutions absorb oxygen and become green, yielding a green precipitate of *bilverdin*, $C_{16}H_{18}N_2O_4$, on addition of an acid. Bilifuscin and biliprasin are obtained as very dark green amorphous bodies, insoluble in water. The alkaline solutions of the biliary colouring-matters, when treated with nitric acid, yield successive tints of green, blue, violet, red, and yellow, which serve to indicate the presence of bile in other secretions.

Glycocholic acid, $C_{24}H_{39}O_4{\cdot}NH{\cdot}CH_2CO_2H$, exists in *bile* as a sodium salt, together with the sodium salt of *taurocholic acid*, $C_{24}H_{39}O_4{\cdot}NH{\cdot}CH_2CH_2SO_3H$. To extract them, *ox-gall* is mixed with bone-black to a paste, which is dried on the steam-bath and digested with absolute alcohol, which dissolves the sodium salts together with cholesterin and cholin. Ether is then added, to precipitate the sodium salts. These are dissolved in water, and decomposed by dil. H_2SO_4, which precipitates the glycocholic acid, at first amorphous, but changing into colourless needles. It is sparingly soluble in water, but dissolves in alcohol, though not in ether. The alkali salts are very soluble and sweet. It is characterised by its behaviour with solution of sugar and strong H_2SO_4, which give a purple-red colour (*Pettenkofer's test for bile*). It is an amido-acid, and yields *cholaglycholic acid*, $C_{26}H_{43}NO_5$, when treated with nitrous acid. When boiled with alkalies, glycocholic acid is hydrolysed into glycocine (amido-acetic acid) and *cholic acid*; $C_{26}H_{43}NO_6 + H_2O = CH_2(NH_2){\cdot}CO_2H + C_{24}H_{40}O_5$. Boiling with dilute HCl effects the same change, but converts the cholic acid into *dyslysin*, $C_{24}H_{36}O_3$, an amorphous precipitate, which becomes potassium cholate when boiled with alcoholic KOH.

Taurocholic acid is not precipitated by normal lead acetate, which precipitates the glycocholic acid from ox-gall, and the filtrate gives a precipitate of lead taurocholate on adding basic lead acetate. When this is suspended in water and

decomposed by H_2S, a solution of the acid is obtained, which may be concentrated and mixed with ether, when the acid separates as a syrup which deposits needle-like crystals. Dog's bile yields more taurocholic acid than that of the ox. Taurocholic acid dissolves readily in water and alcohol. It is decomposed, like glycocholic acid, by boiling with alkalies or acids, but it yields *taurine*, $C_2H_7NSO_3$, instead of glycocine ; $C_{26}H_{45}NSO_7 + H_2O = C_2H_7NSO_3 + C_{24}H_{40}O_5$.

Cholesterin, or *cholesterol*, $C_{26}H_{43}{\cdot}OH$, is a crystalline alcohol found in bile, and composing the chief part of *gall-stones* or biliary calculi, from which it may be extracted by boiling with alcohol, which deposits the cholesterin in transparent lustrous plates on cooling. It is insoluble in water, but soluble in ether ; fuses at 145° C. and sublimes at 200° C. It is unchanged by boiling with potash, and yields ethereal salts when heated with the fatty acids in sealed tubes. HCl converts it into *cholesteryl chloride*, $C_{26}H_{43}{\cdot}Cl$, and ammonia into *cholesteramine*, $C_{26}H_{43}{\cdot}NH_2$. When dissolved in petroleum and treated with sodium, it evolves hydrogen and forms crystalline $C_{26}H_{43}{\cdot}ONa$. When moistened with strong HNO_3 and dried, cholesterin gives a yellow residue which becomes red with NH_3. Strong HCl and a little Fe_2Cl_6 give a violet-blue colour with cholesterin on evaporation. Cholesterin occurs in the blood, in brain, in yolk of egg, in cod-liver oil, and in *musk*, the dried secretion of the musk deer. It is also found in sheep's wool together with *isocholesterin*, having the same composition, but crystallising in needles which melt at 138° C. Cholesterin can absorb over 100 per cent. of water, and in this condition is used as an emollient (*lanolin*).

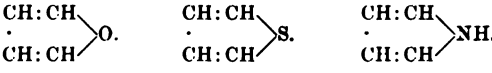
Phytosterin, $C_{26}H_{44}O$, is a similar substance found in peas and other seeds, and in olive oil.

XVI. HETEROCYCLIC COMPOUNDS.

562. Nearly all the compounds hitherto considered have been hydrocarbons or derivatives thereof. There remains a class of substances having closed-chain nuclei, composed not of carbon alone, as are the benzene and naphthalene nuclei, for example, but containing one or more atoms of N, O or S as member or members of the closed chain. Thus they are not strictly derivatives of hydrocarbons. In other respects they might have been considered under the preceding classes, for they are hydrides, alcohols, acids, &c., derived from these *heterocyclic nuclei* instead of from open-chain nuclei or from *carbocyclic nuclei* (like the benzene nucleus).

A few compounds which are strictly within this class have already been described, such as succinic anhydride and the various lactones. These are, however, more of the nature of open-chain derivatives than are those that remain to be discussed. A number of the three and four membered heterocyclic compounds have also received passing notice—*e.g.*, ethylene oxide, trimethylene oxide, diazo-methane, &c. The five- and six-membered* rings of this kind, together with the condensed nuclei corresponding with naphthalene, &c., will now receive attention.

563. **Five-membered heterocyclic compounds.**—The prototypes of these are *furfurane*, *thiophen*, and *pyrrol*, which are believed to possess constitutions expressed by the following formulæ :—



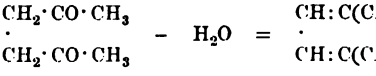
Furfurane. Thiophen. Pyrrol.

They resemble benzene in that they yield derivatives similar to those of that of hydrocarbon, and show little disposition to form addition-

* As in the case of the carbocyclic compounds, 7, 8, &c., membered rings are little known.

products with the halogens. In fact, the arguments which lead to the closed-chain formula for benzene (p. 541) are equally applicable to these compounds.

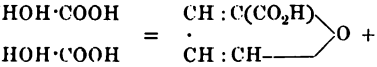
Eloquent of their constitution is their formation from γ-diketones, such as acetonylacetone (p. 647); by dehydration this compound yields 1 : 4-dimethylfurfurane.



With P_2S_5 it yields 1 : 4-dimethylthiophen, and with NH_3 1 : 4-dimethylpyrrol.

Two classes of mono-substitution products are known from these compounds—the α-derivatives, which contain the substituent attached to a carbon atom adjacent to the O, S or N, and the β-derivatives, in which a hydrogen atom of one of the far carbon atoms has been displaced. A third class is possible in the case of pyrrol, for the H of the NH group can be substituted. The possible di-derivatives are more numerous than in the case of benzene; their orientation is expressed by numbering the near carbon atoms 1 and 4, and the far atoms 2 and 3; or by numbering the N, O or S atom 1 and the C atoms 2, 3, 4, 5 successively. A reaction common to all three compounds is the blue colour produced by their reaction with isatin (*q.v.*) and strong H_2SO_4.

Furfurane, C_4H_4O, together with several of its derivatives, is found in the first runnings of the distillation of wood-tar. It is made artificially by distilling pyromucic acid with lime. Pyromucic acid is itself obtained by the destructive distillation of mucic acid (p. 622), thus—



This indicates the constitution of pyromucic acid, and since this acid yields furfurane when distilled with lime it is probably furfurane-carboxylic acid (just as benzoic acid, which yields benzene on distillation with lime, is benzene-carboxylic acid). Thus the constitution of furfurane is settled.

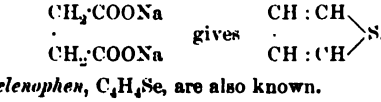
Furfurane is a colourless liquid, smelling of chloroform, insoluble in water and boiling at 32° C. Its aldehyde (furfural) and carboxylic acid (pyromucic acid) have been already considered.

Usnic acid or *pyrotritartaric acid*, $C_4H(CH_3)_2O{\cdot}CO_2H$, found among the products of the destructive distillation of tartaric acid, is α-α_1-dimethylfurfurane-β-carboxylic acid; it is also produced together with *uritic acid* (5 : 1 : 3-*methylphthalic acid*) by heating pyrotartaric acid with baryta water. It melts at 135° C. and decomposes into CO_2 and *dimethylfurfurane*.

Thiophen, C_4H_4S, its homologues and substitution-derivatives, are remarkable for their similarity to benzene, its homologues and derivatives respectively; thus with a large number of benzene derivatives there are corresponding thiophen derivatives of approximately the same boiling-point. Thiophen and its homologues accompany benzene and its homologues in coal-tar, commercial benzene containing about 0.6 per cent. of thiophen. To separate it the benzene is shaken with about 10 per cent. of strong H_2SO_4, which extracts the thiophen as a sulphonic acid. Or the benzene may be heated with mercuric acetate, which forms a complex precipitate with the thiophen, decomposable by HCl into thiophen and $HgCl_2$.

The thiophen passes over when the sulphonic acid is distilled with steam; it is a colourless liquid (sp. gr. 1.06) which smells of benzene, boils at 84° C. and yields a blue colour when mixed with isatin and strong H_2SO_4; this reaction—due to the formation of *indophenin*, $C_{12}H_7NOS$—serves to detect thiophen or its homologues in benzene.

Several fatty compounds yield thiophen when heated with P_2S_3; sodium succinate, for example—



Derivatives of *selenophen*, C_4H_4Se, are also known.

Pyrrol, C_4H_4NH, is a secondary amine and therefore a feeble base. It occurs in coal-tar and Dippel's oil (*q.r.*), from which it may be extracted by H_2SO_4 and distilled over from the sulphates of the stronger bases: it still contains nitriles of fatty acids and benzene hydrocarbons, and is separated from these by heating with solid KOH, which converts it into C_4H_4NK, decomposable into KOH and C_4H_4NH by water.

It is a liquid of chloroform odour, sparingly soluble in water, boiling at 131° C., of sp. gr. 0.97 and becoming brown in air. Hot dilute acids convert it into *pyrrol-red*, $C_{12}H_{14}N_2O$. Pyrrol imparts a fiery red colour to pine-wood moistened with HCl; hence its name. It readily polymerises, hydrogen chloride precipitating $(C_4H_5N)_3HCl$ from its ethereal solution.

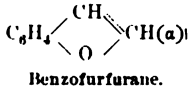
Succinimide yields pyrrol when distilled with zinc dust, and ammonium mucate yields it when distilled alone; it is also formed when a mixture of C_2H_2 and NH_3 is passed through a red-hot tube. Pyrrol treated with $2NH_2OH$ yields *succino-dialdoxime*, $(CH_2{\cdot}CH:N{\cdot}OH)_2$.

There are 3 mono-substitution products from pyrrol, because the H in the NH group may be displaced, yielding *n*-derivatives, besides the *c*-derivatives. The *n*-alkyl pyrrols are obtained from C_4H_4NK and alkyliodides.

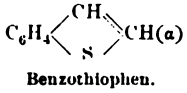
Iodopyrrol, C_4I_4NH, is an odourless substitute for chloroform.

Several *hydropyrrols* and their derivatives are known; *pyrroline* is *α-β-dihydro-pyrrol*, C_4H_6NH; *pyrrolidine* is *tetrahydropyrrol*, or *tertramethyleneimide*, $[CH_2{\cdot}CH_2]_2:NH$.

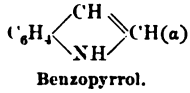
564. **Condensed Nuclei from the Five-membered heterocyclic Compounds.**—These are believed to consist of one or two benzene nuclei condensed with a furfurane thiophen, or pyrrol nucleus, just as naphthalene consists of two, and anthracene of three benzene nuclei condensed together. They are probably represented by the following formulæ—



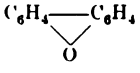
Benzofurfurane.



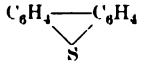
Benzothiophen.



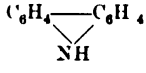
Benzopyrrol.



Dibenzofurfurane.



Dibenzothiophen.



Dibenzopyrrol.

Those derived from one benzene nucleus are formed by treating the corresponding chloro-styrolene with alkali, $C_6H_4\begin{cases}CH:CHCl\\XH\end{cases}$ gives $C_6H_4\begin{cases}CH\\X\end{cases}CH$, where X = O, S or NH.

Benzofurfurane or *coumarone* is a product of the action of alcoholic KOH on coumarin (p. 611); it is found in coal-tar and boils at 177° C. *Coumarilic* acid is its α-carboxylic acid.

Benzothiophen melts at 31° C. and boils at 221° C.

Benzopyrrol or **indol** is the most important member of the group, as it is constitutionally the parent substance of indigo. It may be obtained by distilling reduced indigo (*q.r.*) with zinc dust, and by reducing *o*-nitro-cinnamic aldehyde with Zn and KOH—

$$C_6H_4\begin{cases}CH{\cdot}CHO\\NO_2\end{cases} + H_7 = C_6H_4\begin{cases}CH\\NH\end{cases}CH + 3H_2O.$$

It crystallises in colourless prisms (m.-p. 52° C.) of disagreeable odour, and may be distilled in a vacuum or with steam. It is soluble in water and has weak basic properties, forming a sparingly soluble hydrochloride. A shaving of deal moistened with HCl and exposed to its vapour gives the pyrrol red colour. The hydrochloric solution is coloured red by potassium nitrite. Indol is produced by the action of the peculiar ferment of the pancreatic juice upon the albumin of blood or eggs, and the indican occasionally present in the urine appears to be formed from it.

Many derivatives of indol are known, but only the most important can receive notice here. The orientation of the substitution derivatives is expressed by the

letters α, β, n in the pyrrol ring (*cf.* formula above) and by the numbers 1, 2, 3, 4 in the benzene ring; or by numbering the N atom 1 and the C atoms successively 2 and 3 in the pyrrol ring, and 4, 5, 6, 7 in the benzene ring. Py-1, 2, 3 and Bz-1, 2, 3, 4 are obvious variations.

The *alkylindols* are obtained by heating phenylhydrazones of aldehydes or ketones with HCl or $ZnCl_2$, nucleal condensation occurring with evolution of NH_3. Thus, *β-methylindol* or *skatol* is formed when propionic aldehyde phenylhydrazone is so treated—

$$C_6H_5NH{\cdot}N : CH{\cdot}CH_2{\cdot}CH_3 = C_6H_4\begin{cases}CMe\\NH\end{cases}\!\!>CH + NH_3.$$

Skatol is also a product of the pancreatic fermentation of albumin, and is the chief constituent of the volatile portion of human excrement (*σκατός, of dung*). It crystallises from hot water in colourless plates, melts at 95°, boils at 265° C., and has a fæcal odour. Skatol is found among the products of the distillation of strychnine with lime, and in the wood of *Celtis reticulosa*, a plant of the Nettle-tree order.

Indoxylic acid is *β-hydroxyindol-α-carboxylic acid*, and is obtained as its ethyl salt by heating ethyl *o*-phenylglycocinecarboxylate with sodium ethoxide—

$$C_6H_4\begin{cases}COOEt\\NH{\cdot}CH_2CO_2Et\end{cases} = C_6H_4\begin{cases}C(OH)\\NH\end{cases}\!\!>C{\cdot}CO_2Et + EtOH.$$

The free acid is obtained by heating the ethyl salt with fused NaOH, dissolving in water and precipitating by acid; when heated with alkali and air it yields indigo. It is sold as *indophor* for cotton printing, since it is readily converted into indigo by oxidation on the fibre.

Indoxyl is *β-hydroxyindol* and is produced by heating indoxylic acid, which loses CO_2, also by heating indigo with KOH in absence of air. It is an oily liquid, soluble in water to a yellow fluorescent solution. In alkaline solution it is easily oxidised to indigo, $2C_8H_7ON + O_2 = (C_8H_5ON)_2 + 2H_2O$.

The indoxyl derivatives are either from β-hydroxyindol or the pseudo-form—viz., $C_6H_4\begin{cases}C(OH)\\NH\end{cases}\!\!>CH$ or $C_6H_4\begin{cases}CO\\NH\end{cases}\!\!>CH_2$, respectively. The *indogenides* are derivatives of the latter form in which the $=CH_2$ group has condensed with a $=CO$ group of an aldehyde or ketone to form a $=C=C=$ nucleus.

Indoxyl occurs in the form of *potassium indoxyl-sulphonate* in the urine (*urine-indican*) of herbivora.

α-Methylindolin, $C_6H_4\begin{cases}CH_2\\NH\end{cases}\!\!>CH{\cdot}CH_3$, is a liquid boiling at 227° C., obtained by reducing α-methylindol with Sn and HCl; by carrying the reduction further, with HI and P, *o*-propylaniline is produced. It will be seen that this compound is a methyl-derivative of dihydroindol, which does not exist; the oxygenated dihydroindols, however, are known and are closely related to indigo. They are called *indolinones* and are lactams of amidophenylacetic acid and its homologues (p. 679). They are also obtained by heating the phenylhydrazides (p. 686) of the acids with lime (see oxindol).

Oxindol, or *α-indolinone*, has been already noticed (p. 679); it is produced when acetylphenylhydrazide is heated with lime—

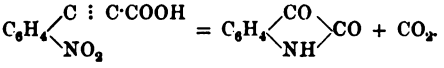
$$C_6H_5NH{\cdot}NH{\cdot}COCH_3 = C_6H_4\begin{cases}CH_2\\NH\end{cases}\!\!>CO + NH_3.$$

It melts at 120° C. and is easily oxidised to *dioxindol* or *β-hydroxyoxyindol*, which in its turn may be oxidised to isatin.

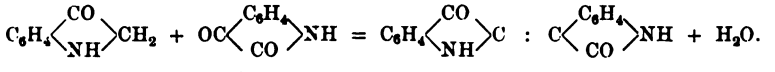
Isatin, $C_6H_4\begin{cases}CO\\NH\end{cases}\!\!>CO$, or $C_6H_4\begin{cases}CO\\N\end{cases}\!\!>C{\cdot}OH$, is prepared by oxidising indigo with nitric or chromic acid. It crystallises in orange-coloured prisms (m.-p. 201° C.), soluble in boiling water and alcohol. When heated, it sublimes with partial decomposition. It dissolves in KOH to a violet solution, and is precipitated again by acids. $AgNO_3$ added to the potash solution gives a carmine-red crystalline

precipitate of *silver isatin*, $C_8H_4AgNO_2$. Isatin forms crystalline compounds with $NaHSO_3$ (like the aldehydes and ketones). It yields aniline when distilled with strong KOH. With chlorine it yields *chlorisatin* and *dichlorisatin*, also formed when chlorine acts on indigo. When these are distilled with KOH, they yield mono- and di-chloraniline. Reducing agents convert isatin into *hydro-isatin*, or *isatide*, $C_{16}H_{12}N_2O_4$, and then into dioxindol and oxindol.

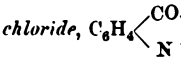
Isatin is also produced by treating *o-nitrophenylpropiolic acid* with alkali—



Isatin condenses with indoxyl under action of alkalies to form the isogenide (*r. s.*) *indirubin*, an isomeride of indigo;

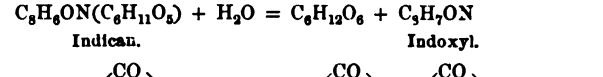


Indoxyl. Isatin. Indirubin.

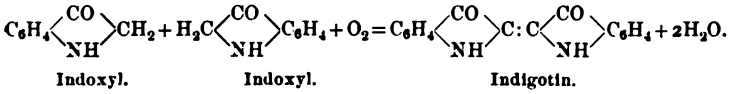
Isatin reacts with PCl_5 in benzene, yielding *isatin chloride*,  , the formula for which supports the second formula given above for isatin. When this chloride is reduced it yields indigo-blue.

565. **Indigotin or indigo blue, $C_{16}H_{10}N_2O_2$,** is prepared from *Indigofera tinctoria* and *cærulea*, plants of the same natural order (Leguminosæ) as those furnishing the dye-woods described on p. 747, and like the colours obtained from those, it does not exist as such in the plant, but is a product of alteration of a nearly colourless substance termed *indican*. *Woad* (*Isatis tinctoria*), a crucifer, also yields indigo.

Indican may be extracted from the leaves and twigs of the plant by digestion with cold alcohol, which leaves it, when evaporated, as a brown, bitter, syrupy liquid. It appears to be a glucoside of indoxyl and is hydrolysed by fermentation or by boiling dilute acids into indoxyl and a glucose called *indiglucin*. The indoxyl is rapidly oxidised by the air into indigotin, which forms a blue precipitate—



Indican. Indoxyl.



Indoxyl. Indoxyl. Indigotin.

For the preparation of indigo on the large scale, the plants are cut just before they blossom, chopped up, covered with cold water, and allowed to ferment for twelve or fifteen hours, when the indican is hydrolysed as explained above. As soon as a blue scum appears upon the surface, a little lime is added, and the yellow liquid is run into shallow vats and well beaten with sticks to promote the action of air, which oxidises the indoxyl. The indigo-blue is precipitated and collected, on calico strainers, to be pressed and cut up into cakes. As purchased, indigo-blue contains about half its weight of indigotin; it may be purified by boiling, first, with acetic acid, which extracts a substance termed *indigo-gluten*, then with weak potash, to extract *indigo-brown*, and, lastly, for some time with alcohol, which removes *indigo-red*.

Indigotin may be prepared from commercial indigo by boiling it with aniline, or heating it with melted paraffin; both solvents deposit the indigotin in dichroic, rhombic crystals on cooling. From hot turpentine it crystallises in blue tables and from fused phthalic anhydride in needles

When commercial indigo is carefully heated, it is converted into a violet vapour, the sp. gr. of which settles the molecular formula for the compound. The vapour condenses in dark blue needles, with a coppery reflection. The best indigo-blue floats upon water.

Indigotin is insoluble in water, alcohol, ether, and diluted acids and alkalies. Strong sulphuric acid and, more easily, fuming sulphuric acid, dissolve it, forming *indigotin-monosulphonic acid*, $C_{16}H_9(SO_2{\cdot}OH)N_2O_2$, and *indigotin-disulphonic* or *sulphindylic acid*, $C_{16}H_8(SO_2{\cdot}OH)_2N_2O_2$.

On adding water, a blue precipitate of the mono-acid is obtained, which is soluble in pure water and in alcohol. It is mono-basic, and its concentrated solution gives a purple precipitate of the potassium salt on addition of potassium acetate. The precipitate produced by K_2CO_3 in the solution of indigo in H_2SO_4 is known as *indigo-carmine*, and consists chiefly of *potassium sulphindylate*; it is soluble in water. The sulphonic acids of indigo are bleached by zinc-dust, being converted into the corresponding acids of indigo-white, which become blue again when shaken with air. Sulphindylic or *sulphindigotic* acid is used in dyeing *Saxony blue* cloth.

Indigo-white (*leucindigo* or *hydrindigotin*) is prepared by shaking powdered indigo with 2 parts of ferrous sulphate, 3 parts of slaked lime, and 200 parts of water, in a stoppered bottle placed in warm water, till the indigo has dissolved to a yellow liquid, when the calcium sulphate and ferroso-ferric hydroxide are allowed to subside, and the clear solution drawn off into dilute hydrochloric acid in a vessel from which air has been expelled by CO_2. The hydrindigotin is precipitated in white flakes, which quickly become blue indigo when exposed to air. Other reducing-agents are sometimes substituted for ferrous sulphate in preparing the dyer's *indigo-vat*. A mixture of indigo, madder, potassium carbonate, and lime, left to ferment, gives an alkaline solution of *reduced indigo*. Hydrosulphites (p. 237) and lime, or zinc-dust and alkali, are also employed for this purpose, and it has been suggested to apply electrolysis for the reduction. When linen and cotton are immersed in the indigo-vat and exposed to air, the indigo-white is oxidised to indigo-blue, which is precipitated upon the fabric. Hydrindigotin precipitated by acids from its alkaline solutions becomes crystalline after a time; it is soluble in alcohol and ether. It probably is of the same form as indigotin, but containing OH groups in place of the O atoms.

When indigo is heated with dilute HNO_3, it is oxidised into isatin, which gives a yellow solution, and sulphindylic acid is sometimes employed as a test for HNO_3. By fusion with KOH it is converted, first into potassium anthranilate, and afterwards into aniline, which distils.

566. **Artificial indigo.**—The unremitting skill and labour which have been concentrated during the last 20 years on the attempt to make indigo from materials the cost of which would be comparable with that of cultivating the indigo plant, have at length succeeded. It may now be said that indigo is made from coal, wood and air, and that the cultivation of the plant is a doomed industry.

Naphthalene and ammonia from coal, acetic acid from wood and oxygen from air are the immediate raw materials for the manufacture: sulphuric acid, chlorine, mercury and alkali are used as agents, but these may be recovered and returned to the process.

The naphthalene is oxidised to phthalic anhydride, which is converted by NH_3 into phthalimide. When the latter compound is

oxidised in alkaline solution by chlorine it yields anthranilic acid, which is then condensed with chloracetic acid to produce phenylglycocine-*o*-carboxylic acid. This acid is heated with alkali to transform it into indoxyl, which yields indigo when treated with air in alkaline solution.

The operations are as follows :—

(1) The oxidation of the naphthalene is effected by atmospheric oxygen, not directly, but by heating the naphthalene in presence of mercury with sulphuric acid of 100 per cent. strength—most conveniently made by combining SO_2 with atmospheric oxygen by the catalytic method (p. 229), and dissolving the SO_3 in water. The mixture is distilled at 300° C. ; phthalic anhydride passes over and CO_2 and SO_2 escape ; the latter is oxidised to sulphuric acid in the manner indicated and used again, thus conveying O from the air to the naphthalene. The mercury dissolves to sulphate and aids the reaction ; the sulphate remains in the retort and is used again.

(2) The phthalic anhydride is treated with NH_3 under pressure when it becomes phthalimide.

(3) The phthalimide is heated in a solution of alkali into which chlorine is passed (sodium hypochlorite).

(4) The solution of alkali anthranilate thus obtained is boiled for some hours with mono-chloracetic acid and Na_2CO_3 in a vessel provided with a reflux condenser ; the solution is then acidified, whereupon crystals of phenylglycocine carboxylic acid separate as the liquid cools.

(5) This acid is heated with NaOH in a closed vessel at 200° C. until the orange colour no longer increases in intensity.

(6) The fused mass, containing indoxyl, is quickly cooled, dissolved in water and air is passed through the solution to precipitate indigo ; if the precipitate is too crystalline it is dissolved in sulphuric acid and precipitated by adding water.

The following equations explain the chemistry of these processes :—

(1) $C_6H_4\begin{<}{CH:CH}{CH:CH}\rangle + O_2 = C_6H_4\begin{<}{CO}{CO}\rangle O + 2CO_2 + 2H_2O.$

(2) $C_6H_4\begin{<}{CO}{CO}\rangle O + NH_3 = C_6H_4\begin{<}{CO}{CO}\rangle NH + H_2O.$

(3) $C_6H_4\begin{<}{CO}{CO}\rangle NH + NaOCl + 3NaOH = C_6H_4\begin{<}{COONa}{NH_2} + NaCl + Na_2CO_3 + H_2O.$

(4) $C_6H_4\begin{<}{COONa}{NH_2} + CH_2Cl{\cdot}COOH + Na_2CO_3 = C_6H_4\begin{<}{COONa}{NH{\cdot}CH_2{\cdot}COONa} + NaCl + CO_2 + H_2O.$

(5) $C_6H_4\begin{<}{COOH}{NH{\cdot}CH_2COOH} + 2NaOH = C_6H_4\begin{<}{CO}{NH}\rangle CH_2 + Na_2CO_3 + 2H_2O.$

(6) The equation for the oxidation of indoxyl has been given above.

It is probable that the process will shortly be simplified, for it has been found that the product obtained by heating anthranilic acid with a polyatomic alcohol or a carbohydrate and KOH yields indigo when treated with water and oxidised.

Another promising method consists in heating phenylglycocine, made from aniline and mono-chloracetic acid, with sodamide.

567. It is proposed to synthesise indigo from aniline by first heating it with CS_2 to produce thiocarbanilide (p. 672) ; the aqueous solution of this is to be heated with white lead and KCN, of which the former appropriates the S, while the latter introduces a cyanogen group, the product being a *hydrocyanocarbodiphenylimide*, which becomes a thioamide by treatment with $(NH_4)_2S$. The thioamide is to be heated with strong H_2SO_4 to produce the anilide of isatin, and this is to be reduced with $(NH_4)_2S$ when it yields aniline and indigo :—

$C_6H_5NH\diagdown\diagup CS$; $C_6H_5NH\diagdown\diagup C{\cdot}CN$; $C_6H_5NH\diagdown\diagup C{\cdot}SNH_2$; $C_6H_4\begin{<}{CO}{NH}\rangle C{:}NC_6H_5$.

Thiocarbanilide. Cyanogen derivative. Thioamide. Isatin anilide.

568. Other methods of synthesising indigo are now only of academic interest either because the yield is too small or because the raw materials are too costly.

From aniline it has been synthesised by heating the base with chloracetic acid to produce phenylglycocine, which yields indigo when heated with fused NaOH and afterwards treated with air. The fusion converts the phenylglycocine into indoxyl.

From benzaldehyde the synthesis is by way of dissolving 1 : 2-*nitrobenzaldehyde* in acetone and adding NaOH, whereupon indigotin is precipitated. It is probable that the first action of the acetone and soda is to convert the 1 : 2-nitrobenzaldehyde into 1 : 2-*nitrophenyl-lactomethyl ketone*; $C_6H_4(NO_2)\cdot CHO + CH_3\cdot CO\cdot CH_3 = C_6H_4(NO_2)\cdot CH(OH)\cdot CH_2\cdot CO\cdot CH_3$. This then breaks up into indigotin, acetic acid and water under further action of NaOH; $2[C_6H_4(NO_2)\cdot CH(OH)\cdot CH_2\cdot CO\cdot CH_3] = C_{16}H_{10}N_2O_2 + 2CH_3\cdot CO_2H + 2H_2O$. The ketone has been sold as its $NaHSO_3$ compound (p. 625), under the name *indigo salt* for printing on the fabric, which is then immersed in a bath of caustic soda.

When cinnamic acid is treated with nitric acid, it is converted into *nitrocinnamic acid*. This combines directly, with two atoms of bromine, to form *dibromo-nitro-phenyl-propionic acid*, $C_6H_4(NO_2)\cdot CHBr\cdot CHBr\cdot CO_2H$. When this is treated with caustic soda, two molecules of HBr are removed, producing the sodium salt of *nitrophenylpropiolic acid*, $C_6H_4(NO_2)\cdot C : C\cdot CO_2H$. By heating this with an alkali and a reducing-agent, it is converted into indigotin.

569. *Dibenzofurfurane* (p. 759) is identical with *diphenylene oxide* and is obtained by distilling phenol with PbO. It melts at 81° and boils at 288° C.

Dibenzothiophen is *diphenylene sulphide*, obtained by heating phenyl sulphide; m.-p. 97°, b. p. 333° C.

Dibenzopyrrol is identical with *carbazole* (p. 667).

570. **Azoles.**—Within the last few years a large class of compounds has been discovered the members of which are regarded as derived from furfurane, thiophen and pyrrol by substitution of a trivalent N atom for a trivalent CH member of the ring, and are known as mono-, di- or tri-azoles accordingly as 1, 2, or 3 of the CH members have been exchanged for N.

By one system, the azoles are distinguished by the prefixes *furo-*, *thio-*, and *pyrro-* to indicate the parent ring, also by the numbers 2, 3, 4, or 5, or the letters a, a_1, b, or b_1, to show which of the four CH members has or have been exchanged. By another system they are classified as *oxazoles*, *thiazoles*, and *pyrazoles*, accordingly as they are allied to furfurane, thiophen, and pyrrol respectively. Condensed azole nuclei, distinguished by the prefix *benzo*, are also known (*cf.* furfurane, &c., p. 757).

Generally speaking, the azoles are products of condensation of aldehydes or ketones with substitution-derivatives of NH_3 or N_2H_4, or H_2NOH.

Pyrazole or *pyrro-2-azole*, $\begin{matrix} CH : N \\ \cdot \\ CH : CH \end{matrix}\!\!>\!NH$, is produced by combining acetylene with diazomethane (p. 680), but better by distilling 3 : 4 : 5-*pyrazole-tricarboxylic acid*, made by condensing ethyl diazoacetate with ethyl acetylenedicarboxylate and saponifying. It is a feeble base, melts at 70° C. and boils at 187° C.

The substituted pyrazoles are nucleal condensation products from the hydrazones of β-diketones. Thus benzoylacetone-hydrazone yields 1 : 3 : 5-*diphenylmethyl-2-pyrazole* :—

$$\begin{matrix} C_6H_5\cdot C\cdot CH_2\cdot CO\cdot CH_3 \\ \cdot\cdot \\ N\!\!-\!\!-\!\!NHC_6H_5 \end{matrix} = \begin{matrix} C_6H_5\cdot C\cdot CH : C\cdot CH_3 \\ \cdot\cdot\quad\cdot \\ N\!\!-\!\!-\!\!N\cdot C_6H_5 \end{matrix} + H_2O.$$

By reduction with Na in alcohol the pyrazoles yield *dihydropyrazoles* derived from $\begin{matrix} CH_2\cdot CH_2 \\ \cdot \\ CH : N \end{matrix}\!\!>\!NH$, and called *pyrazolines*.

Pyrazolones are *ketodihydropyrazoles*, and are important as including the febrifuge **antipyrine** which is 1 : 2 : 3-*phenyldimethylpyrazolone*, $\begin{matrix} CMe\cdot NMe \\ \cdot\cdot \\ CH\!\!-\!\!CO \end{matrix}\!\!>\!NC_6H_5$, prepared by first heating ethyl aceto-acetate with phenylhydrazine to produce phenylmethylpyrazolone, which is then heated with CH_3I in CH_3OH to introduce the second CH_3 group; the alcohol is distilled and the antipyrine precipitated by NaOH. Antipyrine crystallises in white plates, melts at 114° C., dissolves fairly

easily in cold water and is a strong base; its salicylate is sold as *salipyrine* and the homologue in which tolyl takes the place of phenyl, as *tolypyrine*.

Another very complex pyrazolone derivative is the yellow dyestuff *tartrazine*.

The *tetrahydropyrazoles* are called *pyrazolidines*, and the corresponding keto-derivatives are *pyrazolidones*. They are unimportant.

The *indazoles* are *benzopyrazoles* from the isomeric forms $C_6H_4\langle^{CH}_{N}\rangle NH$ and $C_6H_4\langle^{CH}_{NH}\rangle N$, and are so called by analogy with indol, the name given to benzo-pyrrol. Indazole itself has the first form and is made by heating *o*-cinnamic-hydrazide.

The *glyoxalines* are *pyrro*-3-*azoles*, $\begin{matrix}N: & CH\\ \cdot & \\ CH: & CH\end{matrix}\rangle NH$, obtained by condensing α-diketones with NH_3. Several of them, particularly *lophin* (*triphenylglyoxaline*) phosphoresce when decomposed by caustic alkali. *Lysidine*, used as a remedy for gout because of the high solubility of its urate, is a *methyldihydroglyoxaline*.

Isoxazole or *furo*-2-*azole*, and *thiazole* or *thio*-3-*azole*, $\begin{matrix}CH: & N\\ \cdot & \\ CH: & CH\end{matrix}\rangle O$, and $\begin{matrix}N & : CH\\ \cdot & \\ CH: & CH\end{matrix}\rangle S$ respectively, yield a number of derivatives. The *amidothiazoles*, made by condensing chloracetone with thiourea, behave like aniline and may be diazotised to produce thiazole dyestuffs.

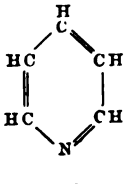
The true diazoles and triazoles of the pyrrol type have sometimes been miscalled triazoles and tetrazoles respectively, the prefix referring to the total number of N atoms.

Thus, *pyrro*-2 : 5-*diazole*, $\begin{matrix}CH: & N\\ \cdot & \\ CH: & N\end{matrix}\rangle NH$, has been called *osotriazole*. Its derivatives are obtained by distilling the osazones of ortho-diketones.

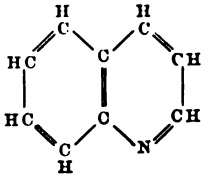
Pyrro-2 : 5 : 4-*triazole* may be either $\begin{matrix}CH: & N\\ \cdot & \\ N & : N\end{matrix}\rangle NH$ or $\begin{matrix}N: & CH\\ \cdot & \\ N: & N\end{matrix}\rangle NH$, and is also known as *tetrazole*.

The derivatives of these compounds as also those of the corresponding oxy- and thio-compounds are at present of theoretical interest only

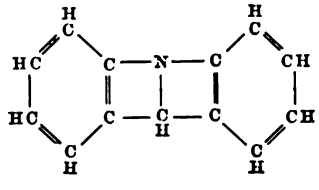
571. **Six-membered heterocyclic compounds.**—The most important members of this class are the substances *pyridine*, *quinoline* and *acridine*. These may be regarded as analogous in constitution to benzene, naphthalene and anthracene respectively, containing, in each case, N in place of CH. This will be clear from the following formulæ:—



Pyridine.



Quinoline.



Acridine.

Their behaviour towards reagents indicates that they are closed-chain compounds (*cf.* benzene, p. 527), and a study of their substitution-products shows that the number of position-isomerides which has been prepared is in accord with that prophesied from the above formulæ.

An inspection of the formulæ shows that there should be three isomeric mono-substituted pyridines, seven isomeric mono-substituted quinolines and five mono-substituted acridines. The orientation is expressed similarly to that of the corresponding hydrocarbons, the N in pyridine and quinoline being 1.

By another system of orientation for pyridine, position $2=\alpha$, $6=\alpha'$, $3=\beta$, $5=\beta'$, and $4=\gamma$; for quinoline $2=\alpha$, $3=\beta$, $4=\gamma$.

572. **Pyridine bases.**—The destructive distillation of bones yields ammonia and other bases, produced by the decomposition of the *bone-gelatine*, or *osséin*, which forms about 30 per cent. of the bones, and contains about 18 per cent. of nitrogen. These bases form an homologous series, of which pyridine is the first member; many of them are also found in coal-tar. They are liquids of disagreeable odour, and are tertiary monamines (p. 658). They may be extracted from the offensive oil known as *Dippel's animal oil*, obtained by distilling bones, by shaking it with warm dilute H_2SO_4, which dissolves the bases as sulphates, and yields them up on adding alkali. They are separated by fractional distillation. Their solubility in water decreases with the increase of C atoms and is generally greater in cold water than in hot.

Pyridine . .	C_5H_5N ... 115° C.	Parvoline . .	$C_9H_{13}N$ ... 188° C.
Picoline . .	C_6H_7N ... 130	Coridine . .	$C_{10}H_{15}N$ ... 211
Lutidine . .	C_7H_9N ... 142	Rubidine . .	$C_{11}H_{17}N$ ... 230
Collidine . .	$C_8H_{11}N$ ... 179	Viridine . .	$C_{12}H_{19}N$ ... 251

Pyridine bases are often present in commercial ammonia, and cause it to become pink when neutralised with hydrochloric acid.

Like other tertiary amines the pyridines combine with alkyl iodides to form *alkylpyridinium iodides*, *e.g.*, $C_5H_5N{\cdot}CH_3I$, and when these are heated they become alkyl-substituted pyridines, *e.g.*, $C_5H_4(CH_3)N{\cdot}HI$, a behaviour similar to that of alkylanilines (p. 664).

Pyridine is a colourless liquid which is soluble in water; it forms a deliquescent hydrochloride, $C_5H_5N{\cdot}HCl$, the solution of which is precipitated by $HgCl_2$, $K_4Fe^{II}Cy_6$ and $PtCl_4$. By the action of sodium in alcohol, pyridine is hydrogenised to *hexahydro-pyridine*, $C_5H_{11}N$, which is identical with piperidine (*v.i.*) and may be reconverted into pyridine by heating at 300° C. with H_2SO_4—

$$C_5H_{11}N + 3H_2SO_4 = C_5H_5N + 3SO_2 + 6H_2O.$$

This conversion of pyridine into piperidine establishes the constitution of the former, that of the latter being known. Pyridine is obtained by heating ammonium nitrate with P_2O_5, which removes the elements of water: $C_5H_{11}NO_3 = 3H_2O + C_5H_5N$. It is also formed when a mixture of hydrocyanic acid and acetylene is passed through a red-hot tube. $HCN + 2C_2H_2 = C_5H_5N$. Like benzene, pyridine resists oxidation in high degree.

Pyridine has been suggested as a remedy for asthma: on the Continent it is used for denaturing alcohol.

The *alkylpyridines* may be obtained by distilling the aldehyde-ammonias, either by themselves or with aldehydes or ketones. Thus acrolein-ammonia yields 3-*methylpyridine* (*picoline*), which is also obtained by heating glyceryl tribromide in a sealed tube at 250° C. with alcoholic NH_3; $2C_3H_5Br_3 + NH_3 = 6HBr + C_6H_7N$. The alkylpyridines are readily oxidised to pyridinecarboxylic acids.

The *hydroxy-pyridines* behave in a manner which leaves it doubtful whether they are really phenolic or ketonic compounds (*pyridones*; *cf.* phloroglucol, p. 716).

Hexahydropyridine or *piperidine*, $C_5H_{11}N$, obtained by reducing pyridine with Na and boiling alcohol, or electrolytically, may be regarded as *pentamethylenimide*, for it is obtained by distilling the hydrochloride of pentamethylene diamine—

$$CH_2\begin{<}{CH_2{\cdot}CH_2{\cdot}NH_2 \atop CH_2{\cdot}CH_2{\cdot}NH_2} = CH_2\begin{<}{CH_2{\cdot}CH_2 \atop CH_2{\cdot}CH_2}\!\!>NH + NH_3.$$

It is a secondary amine, boiling at 106° C., smelling of pepper and NH_3, soluble in water and forming crystalline salts (*cf. piperine*). It combines with alkyl iodides to form *alkylpiperidinium iodides*.

573. **Quinoline bases.**—These may be regarded as *benzo-pyridines*. They occur in bone oil and in coal-tar, and are products of the distillation of many alkaloids with KOH. They form an homologous series, quinoline being the lowest member:—*Quinoline*, C_9H_7N; *lepidine*, $C_9H_6(CH_3)N$; *cryptidine*, $C_9H_5(CH_3)_2N$.

The quinoline bases are synthetically prepared (*Skraup's method*) by heating aniline and its homologues with glycerine, a dehydrating-agent (conc. H_2SO_4) and an oxidant (nitrobenzene);

$$C_6H_4\begin{<}{H \atop NH_2} + \begin{>}{CH_2(OH) \atop CH_2(OH)}CH(OH) + O = C_6H_4\begin{<}{CH:CH \atop N:CH} + 4H_2O.$$

This synthesis shows that the N atom in quinoline must be attached to a benzene nucleus; that it occurs in a pyridine ring is proved by the fact that when quinoline is oxidised with $KMnO_4$, 5 : 6-pyridine dicarboxylic acid (*quinolinic acid*), $C_5H_3(CO_2H)_2N$, is formed (*cf.* the deduction drawn concerning the constitution of naphthalene from the oxidation of the hydrocarbon to phthalic acid).

Quinoline, or *chinoline*, is prepared by the action of H_2SO_4 (50 parts) and nitrobenzene (12 parts) upon aniline (19 parts) and glycerine (60 parts). The mixture is cautiously heated at 130° C. in a flask with a reflux condenser, the lamp being removed when the reaction begins; it is then again heated for three hours, and distilled with lime, when quinoline distils over together with aniline; the latter is converted into phenol by the diazo-reaction (p. 681) and the mixture again distilled with alkali when quinoline passes over. It is a colourless liquid of tarry smell, of sp. gr. 1.09 and boiling-point 239° C. It is sparingly soluble in water, and is a tertiary amine; it forms a sparingly soluble chromate. It combines with alkyl iodides to form *alkylquinolinium iodides* which, when heated with potash, yield blue dyestuffs termed *cyanines*, used in orthochromatic photography. Quinolinic derivatives are very numerous; a few only can be considered.

2-Methylquinoline or *quinaldine* (b.-p. 247° C.) is synthesised by boiling paraldehyde and aniline with HCl. By substituting other aldehydes for paraldehyde, the reaction becomes a general one for preparing alkylquinolines. *4-Methylquinoline* or lepidine boils at 257° C. Both occur in coal-tar and the CH_3 group in each shows a remarkable tendency to react with aldehydic and ketonic compounds. Quinaldine combines in this manner with phthalic anhydride, forming *quinoline yellow*, a dyestuff, $(C_9H_6N)CH:(C_2O_2)C_6H_4$.

Carbostyril is *2-hydroxy-quinoline* and is prepared by dehydrating *o-amido-cinnamic acid*, $C_6H_4\begin{<}{CH:CH\cdot CO_2H \atop NH_2} = C_6H_4\begin{<}{CH:CH \atop N:C(OH)} + H_2O$, and by treating *acetamidobenzaldehyde* with NaOH. It melts at 199° C.

The *tetrahydroquinolines*, $C_9H_{11}N$, are produced by reducing the quinolines with nascent H. They behave like fatty amines, readily forming nitroso- and diazo-derivatives. That obtained by reducing carbostyril boils at 224° C. and yields with methyl iodide the compound *kairolin*, $C_9H_{10}N\cdot CH_3$, the hydroxy-derivative of which is *kairine*, $C_9H_9(OH)N\cdot CH_3$; these two substances and *thalline*, $C_9H_9(OCH_3)NH$ are used as substitutes for quinine.

574. *Isoquinolines* yield 4 : 5-pyridine-dicarboxylic acid when oxidised, showing that the N atom is in the 2-position of the naphthalene ring, $C_6H_4\begin{<}{CH:CH \atop CH:N}$.

Isoquinoline accompanies the quinoline from coal-tar and is separated therefrom by fractionally crystallising the sulphates. It melts at 23° C. and boils at 240·5° C. When a mixture of it with quinaldine is treated with benzotrichloride, *quinoline red*, a dyestuff used in making orthochromatic photographic films, is obtained (*cf.* method of making malachite green, p. 722).

Naphthoquinoline, $C_{13}H_9N$, and *anthraquinoline*, $C_{17}H_{11}N$, are obtained by substituting naphthylamine and amidoanthracene, respectively, for aniline in Skraup's reaction (see above). When *m*- or *p*-phenylenediamine is the amine used, a *phenanthroline*, $C_{12}H_8N_2$, is the product. These compounds are bases similar to quinoline and of complex constitution which cannot be discussed here. *Alizarine blue*

is a *dihydroxyanthraquinoline* obtained by applying Skraup's reaction to *m*-amidoalizarin.

Phenanthridine, $C_6H_4{\cdot}CH$ / $C_6H_4{\cdot}N$, bears the same relationship to phenanthrene (p. 554), that quinoline bears to naphthalene, and is obtained by heating *benzylideneaniline*, $C_6H_5CH : NC_6H_5$. It melts at 104° C.

575. **Acridine bases.**—*Acridine*, $C_{13}H_9N$, occurs in crude anthracene, from which it is extracted by dilute acids, yielding a fluorescent solution; potassium bichromate precipitates it. It forms colourless needles, readily sublimes and has a very irritating vapour. It is a feebler base than pyridine and quinoline, but, like these, combines with alkyl iodides to form *acridinium* derivatives. The synthesis that establishes the constitution of acridine is from diphenylamine and formic acid by heating with $ZnCl_2$; *formyldiphenylamine* is first formed and then loses H_2O :—

$$C_6H_5\underset{N}{\overset{CHO}{|}}C_6H_5 = C_6H_4\underset{N}{\overset{CH}{\cdot}}C_6H_4 + H_2O.$$

The dyestuff *chrysaniline* or *phosphine*, obtained as a by-product in making aniline, is meso-p-*amidophenyl-2-amidoacridine*. *Acridine yellow* and *benzoflavine* are also dyestuffs of this series.

576. **Azines.**—Just as the azoles (p. 764) may be regarded as derived from the N-, O-, and S- five-membered heterocyclic rings, by substituting an N atom for a CH group, so the azines are derived by a similar substitution from the six-membered heterocyclic rings. They are either *oxazines*, *thiazines*, or *diazines* (also *triazine* and *tetrazines*) accordingly as they contain O and N, S and N, or N alone. They are further distinguished by the prefixes ortho-, meta-, and para- accordingly as the O and N, S and N, or N and N are in the 1 : 2, 1 : 3 or 1 : 4 positions to each other respectively. Very few of these numerous compounds can be mentioned here.

Phenoxazine is a *dibenzoparoxazine*, $C_6H_4\underset{NH}{\overset{O}{\diagdown\diagup}}C_6H_4$, produced by heating *o*-amidophenol with pyrocatechol; it melts at 148° C. and only deserves notice as the progenitor of the dyestuffs *resorufine*,* $O : C_6H_3 : [NO] : C_6H_3OH$, obtained by heating resorcinol with nitrosophenol and an oxidant to remove H_2, and *gallocyanine*, a more complex derivative made by heating gallic acid with nitrosodimethylaniline; the former dyes red, the latter violet.

To the *dibenzoparathiazines* belongs *thio-diphenylamine*, $C_6H_4\underset{S}{\overset{NH}{\diagdown\diagup}}C_6H_4$, the product of heating diphenylamine with sulphur. It melts at 180° C. and is the parent substance of the *diphenylamine dyes*; thus, by oxidising paraphenylenediamine in presence of H_2S is obtained *Lauth's violet* or *thionine*,

$$NH_2{\cdot}C_6H_3\underset{S}{\overset{N}{\diagdown\diagup}}C_6H_3 : NH.$$

The tetramethyl derivative of this thionine is *methylene blue*, $N(CH_3)_2{\cdot}C_6H_3 : [NS] : C_6H_3 : N(CH_3)_2Cl$, obtained by treating dimethylaniline hydrochloride with sodium nitrite and reducing the isonitroso-dimethylaniline (p. 664) with H_2S: the *dimethyl-para-phenylenediamine*, $C_6H_4(NH_2){\cdot}N(CH_3)_2$, thus produced is then oxidised by Fe_2Cl_6 in presence of the excess of H_2S; the blue solution is next saturated with NaCl, and $ZnCl_2$ is added to precipitate the $ZnCl_2$ compound of the dyestuff, which forms bronze-green crystals, soluble in cold water to a fine blue liquid from which the colour is fixed on cotton with a tannin mordant. The production of *methylene white*, $C_{12}H_7(CH_3)_4N_3S$, by the action of reducing-agents has led to the use of methylene blue for measuring the reducing power of different portions of the body. The formation of the blue is one of the most delicate tests for H_2S in solution; the liquid to be tested is mixed with excess of HCl, a little dimethyl-para-phenylene diamine sulphate added, followed by a drop of Fe_2Cl_6.

The simplest *metadiazine* is *pyrimidine*, $CH : N{-}CH$ / $CH : CH{\cdot}N$, a soluble base melting at

* It will be noticed that these dyestuffs are represented as containing quinonoid linking (p. 721).

21° C. and boiling at 124° C. The pyrimidines are obtained by heating β-diketones with amidines; they are also products of the polymerisation of alkyl cyanides by sodium at 150° C., and were originally called cyanalkines. Thus *cyanmethine* $(CH_3CN)_3$, from methylcyanide is constitutionally *dimethylamidopyrimidine*; it is a crystalline base having a bitter taste and soluble in water.

The *benzometadiazines* are derivatives of *quinazoline*, $C_6H_4\begin{smallmatrix}CH:N\\ \cdot\\ N:CH\end{smallmatrix}$, not itself known; its α-methyl derivative is produced by treating o-amidobenzaldeyhde with NH_3; it melts at 35° C. and boils at 238° C.

The *paradiazines* are derived from *pyrazine*, $\begin{smallmatrix}CH:N\cdot CH\\ \cdot\ \ \cdot\\ CH:N\cdot CH\end{smallmatrix}$, obtained by distilling amidoacetaldehyde with $HgCl_2$ solution. It melts at 55° and boils at 115° C., but sublimes at the ordinary temperature and smells of heliotrope. *Hexahydropyrazine*, $C_4H_{10}N_2$, is called *piperazine* from its analogy to piperidine; it is a remedy for gout.

Quinoxaline is a *benzoparadiazine*, $C_6H_4\begin{smallmatrix}N:CH\\ \cdot\\ N:CH\end{smallmatrix}$, obtained by heating glyoxal CHO·CHO, with orthophenylenediamine; m.-p. 27°; b.-p. 229° C.

Phenazine is a *dibenzoparadiazine*, $C_6H_4\begin{smallmatrix}N\\ \cdot\\ N\end{smallmatrix}C_6H_4$, obtained by condensing *o*-phenylenediamine with pyrocatechol, $2H_2O$ and H_2 being lost. It crystallises in yellow needles, melting at 171° C. Several important dyestuffs belong to this class; thus the red fluorescent dyestuffs called *eurhodines* are amido-derivatives of *naphthophenazine*, $C_6H_4[N_2]C_{10}H_6$, while the *eurhodoles* are corresponding hydroxy-derivatives. *Toluylene red* is *dimethyldiamidotoluphenazine*,

$$NH_2C_6H_2(CH_3)[N_2]C_6H_3N(CH_3)_2.$$

The **indulines** and **safranines** are dyestuffs which may be regarded as derived from *azoniums*, *i.e.*, the ammonium bases corresponding with the tertiary amines, the azines, such as $C_6H_4:[N\cdot NCH_3Cl]:C_6H_4$. The indulines are mostly blue dyestuffs made by heating *p*-amido-azo-compounds with monamines and an acid, thus—

$$NH_2C_6H_4N:NC_6H_5 + H_2NC_6H_5 = NH:C_6H_3\begin{smallmatrix}N\text{---}\\ \diagdown\\ N(C_6H_5)\end{smallmatrix}\diagup C_6H_4 + NH_3 + H_2.$$

They are of three kinds; the *benzindulenes*, having the above formula derived from phenazine; the *roindulenes*, derived from naphthophenazine; and the *naphthindulines*, derived from *naphthazine*, $C_{10}H_6[N_2]C_{10}H_6$.

The safranines are diamido-derivatives of the azonium salts and may be classified like the indulines. *Tolusafranine*, $NH_2C_6H_3(CH_3):[N\cdot N(C_2H_5)Cl]:C_6H_3NH_2$, the commercial red dyestuff called safranine, is made by oxidising a mixture of *p*-toluylenediamine, *o*-toluidine and aniline.

577. *Pyrone*, $O\begin{smallmatrix}CH:CH\\ \diagup\ \ \diagdown\\ CH:CH\end{smallmatrix}O$, is the only other six-membered ring to which attention can be called; it is a neutral substance obtained by heating *comanic acid*, $C_5H_3O_2\cdot CO_2H$. See meconic acid (p. 622).

Uric Acid and the Alkaloids.

578. **Uric acid and its derivatives.**—Although these are strictly heteronucleal compounds, they are more nearly related to open-chain compounds than are the substances just considered; however, their connection with the vegetable bases, originally all classed together as alkaloids, warrants their discussion at this place.

Uric acid, or *lithic acid*, $C_5H_4N_4O_3$, or $C_2(CO)_3(NH)_4$.—Uric acid is generally prepared from the excrement of the boa-constrictor (*serpent's*

urine from the Zoological Gardens), which consists chiefly of *acid ammonium urate*, $H(NH_4)C_5H_2N_4O_3$; this is dissolved by boiling with dilute potash, which expels NH_3, and converts it into normal *potassium urate*, $K_2C_5H_2N_4O_3$; by passing CO_2 through this, the sparingly soluble *acid potassium urate*, $HKC_5H_2N_4O_3$, is precipitated; this is washed, dissolved in hot water, and decomposed by HCl, which precipitates the uric acid. Human urine also yields uric acid in small crystals when concentrated by evaporation, mixed hot with a little HCl, and set aside: the crystals are much tinged with urinary colouring-matter, and may be purified by dissolving in potash and treating as above; healthy urine yields, at most, one thousandth, by weight, of the acid.

Guano, the partly decomposed excrement of sea-birds, contains much uric acid, which may be extracted from it by boiling it with a 5-per-cent. solution of borax, and adding HCl to the filtered solution.

Uric acid is a white crystalline powder, appearing under the microscope in peculiar modifications of the rhombic prism. It is very sparingly soluble in water, requiring 1800 parts of boiling water and 14,000 parts of cold water; and it is insoluble in alcohol and ether, but dissolves in glycerine and in alkaline liquids.

When heated, it is carbonised and decomposed, emitting odours of NH_3 and HCN; urea and cyanuric acid are also found among the products. Strong H_2SO_4, heated with uric acid, dissolves it without blackening, and, on cooling, deposits crystals containing $2H_2SO_4$; water separates uric acid from them. Nitric acid dissolves uric acid easily when gently warmed, effervescing from escape of N, CO_2, and oxides of nitrogen. On evaporating the solution, the yellow residue becomes red when further heated. This residue is a mixture of several oxidation-products of uric acid, and assumes fine purple colours when treated with NH_3 or KOH (*murexide test*). Uric acid is a reducing-agent; it precipitates cuprous oxide from alkaline cupric solutions, and reduces silver nitrate to the metallic state, if a little Na_2CO_3 is added.

When uric acid is heated with strong hydriodic acid in a sealed tube to 160°–170° C., it yields glycocine, $CH_2NH_2{\cdot}CO_2H$, and the products of decomposition of urea, viz., NH_3 and CO_2. Conversely, if glycocine be heated with excess of urea to 230°, uric acid is formed—

$$CH_2NH_2{\cdot}CO_2H + 3CO(NH_2)_2 = C_2(CO)_3(NH)_4 + 3NH_3 + 2H_2O.$$

Urea is found among the products of distillation and oxidation of uric acid. The acid character of uric acid is feeble, and its salts are, for the most part, sparingly soluble; it is dibasic.

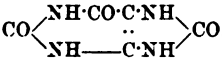
Acid sodium urate, $HNaC_5H_2N_4O_3$, occurs in the gouty concretions termed *chalkstones*, and sometimes as a deposit from urine.

The *acid ammonium urate* is the buff or pink deposit so often formed in urine on cooling; it disappears on gently warming; the colour does not belong to the salt itself. *Acid lithium urate*, $HLi\bar{U}$, is the most soluble urate, requiring 370 parts of cold and 40 parts of boiling water, whilst the sodium salt requires 1100 parts cold and 124 parts boiling, and the ammonium salt requires 1600 parts of cold water.

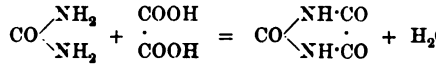
Uric acid and urates are very common constituents of urinary calculi. They are also found in minute quantity in blood and some other animal fluids, and in the solid parts of some animals.

There is no evidence that uric acid contains ·COOH groups, or even ·OH groups; it probably owes its acid character to the presence of : NH groups, which, as has been already explained (p. 669), impart acid properties to compounds containing them. When lead urate is heated with methyl iodide, *dimethyl uric acid*, containing two methyl groups in place of two H atoms, is obtained. This is also a dibasic acid,

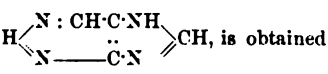
showing that it must still contain two NH groups, and when its lead salt is heated with methyl iodide, *tetramethyluric acid* is obtained. When these methyl uric acids are decomposed, the N appears as methylamine; hence each of the methyl groups is directly united to a nitrogen atom, in which case there must have been four NH groups in the original uric acid. The various decompositions of uric acid, described below, indicate that it contains three carbon atoms directly united, and that at least two of its NH groups must be attached directly to a CO group (for urea, $CO(NH_2)_2$, is a product of its decomposition). These considerations have led to the structural formula for uric acid—

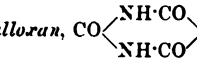


This formula represents uric acid as a *diureide*, a *ureide* being a compound which may be supposed to be formed by condensation of urea with a dibasic acid. Thus parabanic acid (*v.i.*) may be regarded as formed from urea and oxalic acid :—



It will be seen that uric acid contains two urea residues, but the acid of which it is a diureide is not known. The view is supported, however, by the fact that most of its derivatives are of the ureide form.

579. **Purine**,  , is obtained from uric acid by treating it with $POCl_3$ whereby it becomes *trichloropurine*, which yields successively *diiodopurine* and purine when treated with HI and Zn-dust. It melts at 216° C., is very soluble in water and is both an acid and a base. The orientation of the nucleus common to uric acid and purine will be understood from the scheme $2\overset{1\ 6\ 5\ 7}{\text{———}}8$.
$\underset{3\ \ 4\ 9}{\text{———}}$

580. When uric acid is added by degrees to strong nitric acid, it dissolves with effervescence, caused by liberation of CO_2 and N, and the liquid becomes hot. On cooling, it deposits octahedral crystals of *alloxan*,  , or *mesoxalyl-urea*, which stains the skin pink, and gives an intense purple colour with ferrous sulphate and a trace of potash. The octahedral crystals contain 1Aq, but it may be crystallised in prisms with 4Aq.

When alloxan is boiled with baryta-water, it deposits the barium salt of *alloxanic acid*; $C_3O_3(NH)_2CO + H_2O = NH_2{\cdot}CO{\cdot}NH{\cdot}[CO]_2{\cdot}COOH$. If the boiling be long continued, the products are urea and (the barium salt of) *mesoxalic acid*—

$$NH_2{\cdot}CO{\cdot}NH{\cdot}[CO]_2{\cdot}CO_2H + 2HOH = CO(NH_2)_2 + C(OH)_2(CO_2H)_2.$$

By hydrogenising alloxan by passing H_2S through its boiling solution, it is converted into *dialuric acid*, or *tartronyl-urea*, . Dialuric acid crystallises in needles which absorb oxygen when exposed to air, and are converted into *alloxantin*, $C_8H_4N_4O_7$, with loss of $2H_2O$. This body is also precipitated together with sulphur, when H_2S is passed into a cold solution of alloxan, when the dialuric acid formed at first reacts with the excess of alloxan, and the alloxantin, being nearly insoluble in cold water, is removed from the further action of the H_2S.

Alloxantin is precipitated on mixing solutions of alloxan and dialuric acid, so that it is a *diureide* formed from these two ureides by loss of one mol. H_2O. When

uric acid is dissolved in hot dilute nitric acid, alloxantin is the chief product, and its preparation may be combined with that of alloxan by treating the cooled mother-liquor from the alloxan with H_2S, and boiling the precipitate with water, which extracts the alloxantin and deposits it, on cooling, in prisms containing 3Aq. It has an acid reaction, and produces a fine violet precipitate with baryta-water, which is bleached by boiling, being converted into the alloxanate and dialurate. Ferric chloride and a trace of ammonia give a blue colour with alloxantin. It becomes red when exposed to air containing ammonia. On adding ammonium chloride to a hot saturated solution of alloxantin, it becomes first purple and then colourless, depositing a crystalline precipitate of *uramil* (*murexan*) or *dialuramide*, $CO\langle^{NH\cdot CO}_{NH\cdot CO}\rangle CHNH_2$, and leaving alloxan in solution.

If an ammoniacal solution of uramil be mixed with an ammoniacal solution of alloxan, a purple solution is formed which deposits crystals, with a green metallic lustre, of *murexide*, or *acid ammonium purpurate*, $NH_4.C_8H_4N_5O_6.H_2O$. the constitution of which is uncertain, but the formula is the sum of one molecule of uramil, one of alloxan, and one of ammonia. Since alloxan and uramil are both produced when uric acid is evaporated with nitric acid, it is easy to account for the purple colour produced by treating the residue with ammonia.

Murexide is also formed by heating alloxantin to 100° C. in a current of ammonia-gas, when water is eliminated, and by boiling uramil with water and HgO, when an atom of oxygen from the latter acts on 2 mol. of uramil, yielding murexide and water. Murexide is sparingly soluble in cold water, and insoluble in alcohol and ether. Potash dissolves it with a rich purple colour. Acids bleach it, apparently producing uramil.

When alloxantin is heated with strong H_2SO_4, at 100° C., as long as SO_2 is evolved, it is converted into *barbituric acid*, or *malonyl-urea*, which is also obtained synthetically by heating urea with malonic acid and phosphorus oxychloride—

$$3CH_2(CO\cdot OH)_2 + 3CO(NH_2)_2 + 2POCl_3 = 3CH_2\langle^{CO\cdot NH}_{CO\cdot NH}\rangle CO + 2PO(OH)_3 + 6HCl.$$

Barbituric acid is sparingly soluble in cold water. When boiled with alkalies, it yields malonic acid and urea. *Amido-barbituric acid* is identical with uramil.

Parabanic acid, or *oxalyl-urea*, $CO\langle^{NH\cdot CO}_{NH\cdot CO}\rangle$, is the chief product of the more violent oxidation of uric acid, and is prepared by gradually adding uric acid to 6 parts of HNO_3 (sp. gr. 1.3) at 70° C., evaporating to dryness on the steam-bath, and re-crystallising from water. It forms prisms which are strongly acid, dissolve in alcohol, but not in ether. It is a dibasic acid: its solution gives, with silver nitrate, a characteristic crystalline precipitate of $CO:N_2Ag_2(C_2O_2).H_2O$. When boiled with dilute acids, parabanic acid yields urea and oxalic acid, and it may be synthesised from these substances in the presence of phosphorus oxychloride. Most oxidising-agents convert uric into parabanic acid.

Oxaluric acid, $NH_2\cdot CO\cdot NH\cdot CO\cdot CO_2H$, is formed when parabanic acid is boiled with NH_3, ammonium oxalurate crystallising in needles after cooling. If these be dissolved in hot water, HCl precipitates oxaluric acid as a crystalline powder. This acid has the same relation to parabanic acid as alloxanic acid has to alloxan—

Alloxan . .	$N_2H_2(CO)_4$	Parabanic acid .	$N_2H_2(CO)_3$
Alloxanic acid .	$N_2H_3(CO)_3\cdot CO_2H$	Oxaluric acid . .	$N_2H_3(CO)_2\cdot CO_2H$

A small quantity of ammonium oxalurate may be extracted from urine by animal charcoal; after having served for the filtration of a large volume of urine, the charcoal is well washed with water, and boiled with alcohol, which leaves the oxalurate mixed with colouring-matter, when evaporated.

Oxaluramide, $N_2H_3(CO)_2\cdot CO\cdot NH_2$, is metameric with *ammonium parabanate*, $CO\cdot N_2H(NH_4)\cdot C_2O_2$, and is obtained by heating that salt to 100° C.

Dimethyl-parabanic acid, $CO\cdot N_2(CH_3)_2\cdot C_2O_2$, or *cholestrophane*, is formed when silver parabanate is heated with methyl iodide. It is interesting from having been originally obtained by the oxidation of caffeine (see *Caffeine*).

The principal immediate products of the oxidation of uric acid in solution have been seen to be alloxan, parabanic acid, and urea; but, when an alkaline

solution of uric acid in potash is exposed to air, it slowly absorbs oxygen, and deposits crystals of the potassium salt of *uroxanic acid*, from which the acid may be precipitated by HCl; $C_5H_4N_4O_3 + 2H_2O + O = C_3H_6N_4O_2(CO_2H)_2$. When boiled with water, this acid is decomposed into single molecules of CO_2, urea, and *glyoxyl-urea*, $CO\langle^{NH\cdot CO}_{NH\cdot CHOH}$, or *allanturic acid*.

When uric acid is boiled with PbO_2 and H_2O, a precipitate of lead oxalate is formed, and the filtrate deposits crystals of *allantoin*, $C_4H_6N_4O_3$, and urea on evaporation; $2C_5H_4N_4O_3 + O_2 + 5H_2O = C_4H_6N_4O_3 + 2CON_2H_4 + 2C_2H_2O_4$. Allantoin is found in the allantoic liquid of the cow.

Iso-uric acid, having the same composition as uric acid, but more easily oxidised, is deposited on boiling alloxantin with solution of cyanamide—
$C_8H_4N_4O_7$ (*alloxantin*) + $2(CN\cdot NH_2)$ (*cyanamide*) = $2C_5H_4N_4O_3$ (*iso-uric acid*) + O.
Some alloxan is formed at the same time by the oxidation of some of the alloxantin, which thus serves as the necessary reducing-agent.

Uric acid has been synthesised by the following reactions:—

Action of urea on ethyl aceto-acetate yields *methyl uracyl* $CO\langle^{NH\cdot C(CH_3)}_{NH\cdot CO}\rangle CH.$

Action of HNO_3 on this yields *nitrouracylcarboxylic acid* $CO\langle^{NH\cdot C(CO_2H)}_{NH\cdot CO}\rangle CNO_2.$

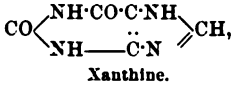
By heating with lime this yields *nitrouracyl* . . . $CO\langle^{NH\cdot CH}_{NH\cdot CO}\rangle CNO_2.$

By reduction this yields *isobarbituric acid* . . . $CO\langle^{NH\cdot CH}_{NH\cdot CO}\rangle COH.$

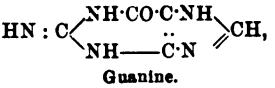
By oxidation this yields *isodialuric acid* . . . $CO\langle^{NH\cdot COH}_{NH\cdot CO}\rangle COH,$

which yields uric acid when warmed with urea and H_2SO_4.

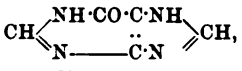
581. Theoretically, the parent of uric acid is purine (p. 771), from which are also derived the bases—



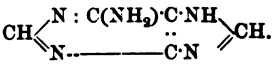
Xanthine.



Guanine.



Hypoxanthine.



Adenine.

These, like uric acid, are products of degradation of the animal organism and are also present in some vegetable products, such as the juice of the beet root. They are all obtainable from uric acid through trichloropurine (*r.* purine, p. 771), which yields these four bases by different reactions. Guanine is converted into xanthine and adenine into hypoxanthine by HNO_2.

Guanine, $C_5H_5N_5O$, is extracted from guano (the excrement of sea-fowl) by boiling it with lime and water, and boiling the undissolved residue with NaOH, which dissolves the guanine and uric acid; these are precipitated by acetic acid, and the guanine dissolved out by hydrochloric acid, and precipitated by NH_3. It is amorphous, insoluble in water and alcohol, and is at once a feeble di-acid base and dibasic acid. It gives the murexide reaction, and when oxidised by $KClO_3$ and HCl, it yields CO_2, parabanic acid, and guanidine—

$$C_5H_5N_5O + O_3 + H_2O = CO_2 + C_3H_2N_2O_3 + C(NH)(NH_2)_2.$$

Guanine is found in the pancreas of the horse, in gouty deposits in pigs, in the excrement of spiders and the scales of bleak. It is formed, together with xanthine and sarcine, when yeast is allowed to decompose in water at 35° C.

Xanthine, $C_5H_4N_4O_2$, is prepared by the action of nitrous acid on guanine: $C_5H_5N_5O + HNO_2 = C_5H_4N_4O_2 + H_2O + N_2$. It forms minute white crystals sparingly soluble in water, insoluble in alcohol, dissolved by alkalies, and reprecipitated by acids. It gives the murexide reaction. Its crystalline salts with acids are decomposed by water. Its ammoniacal solution yields, with $AgNO_3$, a gelatinous precipitate containing $C_5H_2Ag_2N_4O_2.H_2O$, which, when treated with CH_3I, yields theobromine (*q.v.*).

Xanthine occurs in certain rare urinary calculi, and, in small quantity, in urine, in the liver, pancreas, spleen, and brain; also in guano and yeast.

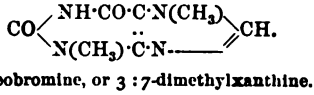
Sarcine, or *hypoxanthine*, $C_5H_4N_4O$, exists in extract of meat, amounting to about 0.6 per cent., and may be precipiated from the mother-liquor of the extraction of creatine (p. 676) by boiling with cupric acetate. The brown precipitate is dissolved in HNO_3 and precipitated by $AgNO_3$, which forms an insoluble compound from which the sarcine may be extracted by decomposing with H_2S and boiling with much water. It crystallises in minute needles, and is more soluble than xanthine, though it forms a less soluble hydrochloride. It is feebly basic and acid. Nitric acid oxidises it to xanthine. Sarcine is generally found together with xanthine, and occurs in many parts of the animal body, especially in marrow.

Adenine, $C_5H_5N_5$, found in the pancreas of the ox and in tea, crystallises in lustrous laminæ (with $3H_2O$) and is soluble in water.

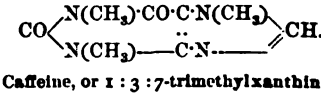
Carnine, $C_7H_8N_4O_3$, is also found in extract of meat, and much resembles xanthine and sarcine. Nitric acid or bromine-water oxidises it to sarcine.

582. **The Alkaloids.**—These compounds possess particular interest for the chemist, on account of their powerful action on the animal economy, many of them being the active principles of the medicinal or poisonous plants from which they are extracted. Hitherto few of them have been prepared artificially, though the study of their properties indicates that they are ammonia-derivatives. They all contain nitrogen, but rarely more than two atoms in a molecule, though there may be twenty or thirty carbon-atoms; they all contain oxygen with the exception of coniine, nicotine, and sparteine, which are volatile liquids. Most of them refuse to sublime without partial decomposition, which unfits them for ranking as *amines;* they dissolve sparingly in water, which renders it unlikely that they are ammonium bases, and brings them nearer to the *amides*, which many of them also resemble in their feebly basic character. The alkaloids are soluble in alcohol, and their solutions are generally alkaline and bitter. Their salts are formed, like those of ammonia, by the direct union of the base and the acid, without separation of water, and, as a rule, the salts are soluble in water. The hydrochlorides of the alkaloids resemble those of all amines, as well as the chlorides of the alkali-metals and the ammonium bases, in forming crystalline double salts with platinic chloride, mercuric chloride, and auric chloride. Most of the alkaloids may be precipitated from their solutions by iodine dissolved in potassium iodide, by potassio-mercuric iodide, by potassio-bismuthic iodide, by picric acid, tannin, metatungstic acid, and phosphomolybdic acid.

583. **Xanthine-alkaloids.**—The alkaloids, *theobromine* and *caffeine*, are methyl derivatives of xanthine:—



Theobromine, or 3 : 7-dimethylxanthine.



Caffeine, or 1 : 3 : 7-trimethylxanthine.

Theobromine, $C_7H_8N_4O_2$, is extracted from the seeds of the cacao tree (*Theobroma cacao*), which grows in Demerara. These are known as *cocoa-nibs*, and are the raw material of cocoa and chocolate. The cocoa-beans contain 1–2 per cent. of theobromine, which may be extracted from them in the same way as caffeine (which it

much resembles) from tea or coffee. When treated with $KClO_3$ and HCl, it yields methylalloxan and methyl-urea. When theobromine is dissolved in ammonia and boiled with silver nitrate, a white precipitate of *silrer theobromine*, $C_7H_7AgN_4O_2$, is obtained, and when this is heated with methyl iodide, it yields *methyl-theobromine*, or caffeine. Theobromine is similarly obtained from silver xanthine (p. 774).

Caffeine or *theine*, $C_8H_{10}N_4O_2$, is extracted from a plant of Cinchonaceous order, the coffee-tree (*Caffea arabica*), the seeds of which contain about 1.5 per cent. of caffeine. It is also found in the leaves; but those of the tea-plant (*Thea*) yield more of it, the proportion in the dried leaf varying from 2 to 4 per cent. To prepare caffeine, tea-dust is boiled with water to extract all the soluble matter, which amounts to about 30 per cent., and consists of tannin, caffeine, aromatic oil, and other bodies. The decoction is filtered, mixed with excess of lead acetate, which precipitates the tannin, again filtered, the lead precipitated by H_2S, and the filtrate from the lead sulphide evaporated to a small bulk, when the caffeine crystallises and may be purified by recrystallisation from alcohol.

The waste tea-leaves which have been exhausted in the tea-pot yield a considerable proportion of caffeine when treated in this way. Caffeine may be similarly extracted from ground unroasted coffee-beans. It may be sublimed from tea-leaves or coffee-beans by gently heating them in an evaporating-dish covered with a dial-glass; one of the best processes for obtaining it is to precipitate decoction of tea with tribasic lead acetate, to evaporate the filtrate to dryness, on the steam-bath, at last, and to cautiously heat the dry residue in an evaporating-dish, when the caffeine sublimes on to the cover.

Caffeine is contained in several plants which are used in various places for chewing or preparing drinks. *Paraguay tea* is made from the leaves of one of the *Ilicaceæ*, or Holly order, the *Ilex paraguayensis*, and is drunk, under the names of *maté* and *congonha*, in Paraguay, Brazil, Chili and Peru. The leaves contain caffeine. Another beverage containing caffeine is used by the Indians of Brazil and called Guaraná, being prepared from the seeds of the *Paullinia sorbilis*, a tree of the Soapwort order, to which the horse-chestnut belongs. The *kola-nut*, or seeds of *Cola acuminata*, used as food and medicine by the natives of West-Central Africa, contains about 2 per cent. of caffeine.

Caffeine crystallises in fine silky needles (with $1H_2O$). It becomes anhydrous at 100° C. and then melts at 233° C., and sublimes undecomposed. It dissolves in 90 parts of cold water, yielding a bitter solution, which is not alkaline. It is soluble in alcohol and ether, and more easily in benzene and chloroform.

Caffeine is a very feeble base, its salts being decomposed by water. The hydrochloride, $C_8H_{10}N_4O_2.HCl.2Aq$, crystallises from strong hydrochloric acid in prisms, which leave pure caffeine at 100° C. The sulphate, $C_8H_{10}N_4O_2.H_2SO_4$, is obtained in needles by adding dilute sulphuric acid to a hot alcoholic solution of caffeine. The acetate is $C_8H_{10}N_4O_2(C_2H_4O_2)_2$.

Chlorine-water (or HCl + $KClO_3$) converts caffeine into *amalic acid*, or *tetramethyl alloxantin*, $C_8(CH_3)_4N_4O_7.Aq$. In the presence of air, water, and ammonia, this yields *murexoin*, or *tetramethyl murexide*, $C_8(CH_3)_4N_5O_6(NH_4)$, which crystallises from hot water in scarlet prisms with a golden lustre. The test for caffeine is based on this: dissolve it in strong HCl, add a crystal of potassium chlorate, and evaporate to dryness. A red residue is left, which becomes purple with ammonia, and is bleached by potash.

The final product of the action of chlorine-water on caffeine is *cholestrophane* (p. 772). When long boiled with baryta-water, caffeine is converted into *caffeidine*, $C_7H_{12}N_4O$, which is a stronger base than caffeine—

$$C_8H_{10}N_4O_2 + Ba(OH)_2 = C_7H_{12}N_4O + BaCO_3.$$

Theophyllin or 1 : 3-*dimethylxanthine* accompanies caffeine in tea; it melts at 264° C.

584. **Pyridine-alkaloids.**—The alkaloids *piperine*, *coniine*, and *nicotine*, are derivatives of pyridine.

Piperine, or *piperidine piperate*, $C_{11}H_9O_2{\cdot}CO{\cdot}NC_5H_{10}$, bears the same relationship to *piperic acid*, $CH_2\langle{}^{O}_{O}\rangle C_6H_3{\cdot}CH:CH{\cdot}CH:CH{\cdot}CO_2H$, that acetamide bears to acetic acid, the piperidine (p. 766) residue, $\cdot NC_5H_{10}$, behaving like the ammonia residue, $\cdot NH_2$. It is a feeble base extracted by alcohol from white pepper, the ripe fruit of *Piper nigrum* (the unripe fruit is black pepper). It crystallises in prisms (m.-p. 128° C.), which are insoluble in water, but soluble in ether. The alcoholic solution tastes hot. When boiled with potash it yields piperidine, and potassium piperate. It dissolves in H_2SO_4, conc. with a red colour.

Coniine, or *2-normal-propyl piperidine*, $C_5H_9(C_3H_7)NH$, is extracted from the seeds of hemlock (*Conium maculatum*) by crushing them and distilling with weak KOH. The distillate, which contains NH_3 and coniine, is neutralised with H_2SO_4, concentrated by evaporation, and mixed with alcohol to precipitate the $(NH_4)_2SO_4$. On evaporating the filtrate and distilling with strong KOH, coniine distils with water, upon the surface of which it floats. It is dehydrated with dried K_2CO_3, and fractionated.

Coniine has a strong odour of mice; its sp. gr. is 0.89, and it boils at 167° C. It is sparingly soluble in cold water, giving an alkaline solution. It dissolves in alcohol and ether. When exposed to air, it becomes brown, and evolves NH_3. Oxidising-agents, such as nitric and chromic acids, convert it into butyric acid. When coniine is heated in a sealed tube with CH_3I, it exchanges H for CH_3, showing it to be a secondary monamine, $NH(C_8H_{16})''$. The *methylconiine*, $NCH_3(C_8H_{16})''$, sometimes occurs in hemlock. It combines with CH_3I to form a crystalline *coniine-methylium iodide*, $N(C_8H_{16})''(CH_3)_2I$, which yields a caustic base when decomposed by AgOH. Hemlock also contains another base, *conhydrine*, $C_8H_{17}NO$, crystallising in plates.

Coniine has been obtained artificially by the action of sodium on an alcoholic solution of *allyl-pyridine*, $C_5H_4(C_3H_5)N$, a liquid product of the action of paraldehyde upon picoline, $C_5H_4(CH_3)N$. The base obtained in this way, however, is optically inactive; when its tartrate is fractionally crystallised, it is split up into a lævo-base and a dextro-base (*cf.* p. 606); the latter is coniine.

Paraconiine, $C_8H_{15}N$, *propyl tetrahydropyridine*, is obtained by distilling the product of the action of alcoholic ammonia on butyric aldehyde—

$$2C_3H_7CHO + NH_3 = H_2O + C_8H_{17}NO$$

(*dibutyraldine*); $C_8H_{17}NO = H_2O + C_8H_{15}N$ (*paraconiine*). This base is very similar to coniine, and, like it, a powerful narcotic poison, but is optically inactive, and appears to be a tertiary monamine.

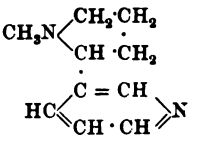
Nicotine, $C_{10}H_{14}N_2$, is found chiefly as malate, in the seeds and leaves of tobacco, *Nicotiana tabacum*, a plant of the order of Atropaceæ, many of which, especially deadly nightshade, thorn-apple, henbane, and mandrake, yield narcotic poisons. Nicotine is extracted from tobacco leaves by digesting them with very dilute H_2SO_4, evaporating to a small bulk, and distilling with excess of KOH. The distillate is shaken with ether, the ethereal layer is drawn off, the ether distilled, and the nicotine placed in contact with quick-lime to remove the water, and distilled in a current of hydrogen, since it is decomposed when distilled in air at the ordinary pressure.

Nicotine is colourless when freshly prepared, but soon becomes brown in air. It smells strongly of tobacco, has sp. gr. 1.01, and boils at 247° C. It is soluble in water, alcohol, and ether; its solution is alkaline. It is a di-acid base, but its salts do not crystallise well. When heated with ethyl iodide, it behaves as a tertiary amine, yielding

nicotine-ethylium di-iodide, $N_2(C_{10}H_{14})''(C_2H_5)_2I_2$, which yields the corresponding caustic base when decomposed by AgOH.

By oxidation with chromic acid, nicotine yields *nicotinic acid* (*pyridine-3-carboxylic acid*) $C_5H_4(CO_2H)N$ which yields *pyridine*, when distilled with lime.

Nicotine is α-pyridyl-*n*-methyltetrahydropyrrol, being obtainable by a somewhat complex series of reactions from the amide of nicotinic acid by introduction of a pyrrol group in place of the $CONH_2$ group.



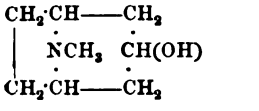
Nicotine.

Virginia tobacco contains more nicotine than other varieties, the alkaloid amounting to nearly 7 per cent. of the weight of the leaf dried at 212° F., whilst the Maryland and Havana varieties contain only 2 or 3 per cent. Tobacco is remarkable for the very large amount of ash which it leaves when burnt, amounting to about one-fifth of the weight of the dried leaf, and containing about one-third of K_2CO_3, resulting from the decomposition of the malate, citrate, and nitrate of potassium during the combustion. The latter salt is frequently present in larger quantity than is found in most other leaves and aids the combustion, for which purpose it is sometimes added; but it is often present only in very small proportion and the burning quality of the tobacco is not impaired by its absence.

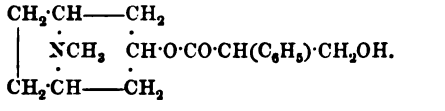
Cigars are made directly from the moistened tobacco leaves which may or may not have undergone a fermentation; but *snuff*, after being moistened, is subjected, in large heaps, to a fermentation extending over 18 or 20 months, when it becomes alkaline from the development of $(NH_4)_2CO_3$ (by the putrefaction of the vegetable albumin in the leaf) and of a minute quantity of free nicotine, which imparts the peculiar pungency to this form of tobacco. The aroma of the snuff appears to be due to the production of a peculiar volatile oil during the fermentation. The proportion of nicotine in snuff is only about 2 per cent., being one-third of that found in the unfermented tobacco; and a great part of this exists in the snuff in combination with acetic acid, which is also a result of the fermentation.

585. *Sparteine*, $C_{15}H_{26}N_2$, is a narcotic alkaloid extracted from the common broom (*Spartium scoparium*) by digestion with weak sulphuric acid and decomposing the sulphate by distilling with potash. It is liquid, heavier than water, boiling at 311° C. It is sparingly soluble in water, giving an alkaline solution with a bitter taste. It smells rather like aniline, and becomes brown when exposed to air. It acts as a di-acid base, and appears to be a tertiary di-amine.

586. **Tropine-alkaloids.**—*Atropine*, *hyoscyamine* and *cocaine* are derivatives of a base *tropine* which behaves as a 1-methyl-4-hydroxypiperidine wherein the 2- and 5-C atoms are linked by a $\cdot CH_2 \cdot CH_2 \cdot$ group. Atropine and hyoscyamine are isomeric forms of a salt of this base with *tropic acid* or *α-phenylhydracrylic acid*.



Tropine.



Atropine.

Tropine, $C_8H_{15}NO$, is a crystalline base melting at 62° C. and boiling at 263° C., obtained by hydrolysis of atropine.

Atropine and **hyoscyamine**, $C_{17}H_{23}NO_3$, are physical isomerides associated in several plants of the order *Solanaceæ*, the former particularly in deadly nightshade (*Atropa belladonna*) and thorn-apple (*Datura stramonium*), the latter especially in *hyoscyamus* (henbane). Both alkaloids have the characteristic (*mydriatic*) effect of dilating the pupil of the eye.

Atropine is obtained by expressing the sap from the flowers of belladonna, heating it to 90° C. to coagulate albumin, filtering, adding KOH to liberate the base, and shaking with chloroform, which collects it and sinks to the bottom. The chloroform is distilled, and the atropine recrystallised from alcohol. It forms prisms, fusing at 115° C., sparingly soluble in cold water, and having a bitter burning taste and a very poisonous action. Atropine is optically inactive and hyoscyamine lævo-rotatory, but the lævo-atropine obtained by resolving the inactive form is not identical with hyoscyamine.

Solanine, $C_{42}H_{87}NO_{16}$, is contained in plants of the same order, especially in *Solanum nigrum* and in the shoots of potatoes (*Solanum tuberosum*) which have been kept in a cellar during winter. To extract it, the plant is digested with weak sulphuric acid, and the solution precipitated with ammonia. It crystallises from alcohol in prisms, which are nearly insoluble in water. It gives a red solution when heated with sulphuric acid and alcohol.

Cocaine, $C_{17}H_{21}NO_4$, is extracted from the leaves of *Erythroxylon coca*, a Peruvian stimulant. It crystallises in prisms, melts at 98° C. and dissolves in alcohol. It is lævo-rotatory and is a valuable local anæsthetic, for which purpose the hydrochloride is sold. When hydrolysed cocaine yields tropine carboxylic acid or *ecgonine*, benzoic acid and methyl alcohol. It is, therefore, a benzoate of methyl tropine carboxylate, and may be represented by substituting the benzoic acid residue for that of tropic acid, and CO_2CH_3 for H in the 3-position of the piperidine ring, in the formula for atropine (*r.s.*).

587. **Opium-alkaloids.**—Opium (ὀπός, *juice*) is obtained from the *Papaver somniferum*, or opium-poppy, cultivated in Turkey, Egypt, India, and other Oriental countries. A few days after the poppy-flower has fallen, incisions are made in the poppy-head, when a milky juice exudes. After twenty-four hours this becomes a soft solid mass of brown colour, and is scraped off and wrapped in leaves for the market. Opium contains about 25 per cent. of a gummy substance, 20 per cent. of ill-defined organic matters, a little caoutchouc, resin, oil, and water, and variable proportions of a large number of alkaloids, of which morphine, narcotine, papaverine, and narceine are the most abundant. Little is known of the constitution of morphine, but the investigation of narcotine, papaverine, and narceine has been more fruitful; the results, however, are too complex for discussion here.

Laudanum is supposed to contain about 7 parts by weight of opium in 100 measures of proof spirit.

Morphine, or *morphia*, $C_{17}H_{19}NO_3$, is extracted from opium (which contains 6–15 per cent.) by steeping it in warm water, which dissolves the meconate and sulphate of morphine, straining, and adding $CaCl_2$, which precipitates calcium meconate. The filtered solution is evaporated to a small bulk and set aside, when the hydrochlorides of morphine, codeine, and oxymorphine crystallise. These are dissolved in water, and the morphine precipitated by adding ammonia. It is recrystallised from alcohol in prisms (with $1H_2O$), which become anhydrous and melt at 120° C. It is almost insoluble in water, requiring 10,000 parts of cold and 500 parts of boiling water, and nearly insoluble in ether and chloroform, both of which dissolve most other alkaloids.

Morphine is soluble in ethyl acetate (acetic ether) and in amyl alcohol, either of which may be employed to extract it from an aqueous solution. Even ether may be employed to extract morphine from an alkaline solution, if shaken with it immediately after adding the alkali, and before the morphine has precipitated. Morphine differs from most other alkaloids by being very soluble in potash: if a drop of weak potash be stirred with solution of a salt of morphine, the alkaloid is precipitated, but it is redissolved by a very little more potash. Ammonia does not easily redissolve it unless NH_4Cl be present.

Morphine behaves like a tertiary monamine; it contains two OH groups and resembles, in some reactions, a phenol-alcohol. Its solutions are alkaline, and it combines with acids, like ammonia.

Morphine hydrochloride, $C_{17}H_{19}NO_3.HCl$, or *muriate of morphia*, is the chief form in which morphine is used in medicine. It crystallises in needles with 3Aq, and is easily soluble in water and alcohol. *Morphine meconate*, the most soluble of the salts, is also used in medicine.

Morphine and its salts act as powerful narcotic poisons; they are easily identified by giving a blue colour with ferric chloride (purple in the case of meconate) and a golden yellow with strong nitric acid. Morphine acts, in many cases, as a reducing-agent; it liberates iodine from iodic acid in solution; it reduces potassium ferricyanide to ferrocyanide, and precipitates silver when boiled with silver nitrate. When distilled with potash, morphine yields methylamine.

Morphine periodide, $C_{17}H_{19}NO_3I_4$, is obtained as a brown precipitate when solution of iodine in KI is added to morphine hydrochloride.

Apomorphine, $C_{17}H_{17}NO_2$, is formed when morphine is heated with a large excess of strong HCl for some hours, at 150° C.; $C_{17}H_{19}NO_3 = C_{17}H_{17}NO + H_2O$. From the hydrochloride thus obtained, Na_2CO_3 precipitates apomorphine as an amorphous powder, rapidly turning green in air, and then dissolving in ether with a pink colour. It is much more soluble in alcohol and ether than is morphine, and is a powerful emetic, even when injected under the skin.

Codeine, *codeia*, or *methyl morphine*, $C_{17}H_{18}(CH_3)NO_3$, is obtained from opium by adding potash or soda to the ammoniacal filtrate from the morphine. It may be purified by crystallisation from ether. Codeine has been obtained from morphine by heating it with methyl iodide in alcoholic solution.

Codeine melts at 150° C. and is easily soluble in hot water, alcohol, and ether. It crystallises from ether in anhydrous octahedra, and from water in rhombic prisms, which contain Aq. The crystals fuse under water. It is a narcotic poison, though less powerful than morphine, and amounts in opium to only about 0.5 per cent. It is strongly alkaline, gives no colour with ferric chloride, and does not reduce iodic acid like morphine. It is a tertiary monamine. When heated with caustic alkalies, it yields methylamine and trimethylamine. Heated with strong HCl at 150° C., it yields apomorphine and methyl chloride.

Narcotine, $C_{22}H_{23}NO_7$, is extracted by digesting with acetic acid the residue left after exhausting opium with water. The narcotine is dissolved and is precipitated on adding NH_3. It crystallises from alcohol in prisms, which contain Aq., but like morphine, is almost insoluble in water; it dissolves in ether, however, which extracts it from powdered opium, leaving the morphine. Narcotine is insoluble in potash, and melts at 176° C. It is a very feeble base, not alkaline, dissolving in acids, but not forming well-defined salts. It has a narcotic effect, but is not nearly so poisonous as morphine. Opium contains usually about 1 per cent. of narcotine, and the presence of this drug is more easily detected by testing for narcotine than for morphine, on account of the solubility of the former in ether. The material to be tested is extracted with ether, the latter evaporated, the residue dissolved in dilute HCl, and a little *euchlorine-water* added (made by adding strong HCl to a weak solution of $KClO_3$ till it has a bright yellow colour, and adding water till it is pale yellow); this produces, with narcotine, a yellow colour in the cold, becoming pink on boiling and adding more of the euchlorine water.

When narcotine is long boiled with water it yields a new base, *cotarnine*, $C_{12}H_{15}NO_4$ (m.-p. 132° C.) soluble in water, and *meconine* or 5 : 6-*dimethoxyphthalide*, $(CH_3O)_2C_6H_4\langle{}^{CO}_{CH_2}\rangle O$, (*phthalide* being the lactone of 1 : 2-methylbenzoic acid). Meconine is sparingly soluble in water and melts at 102° C. It occurs in opium to the extent of 1 per cent. Cotarnine appears to be an oxy-derivative of *n*-methylisoquinoline, containing a methoxy-group. When reduced it yields *hydrocotarnine*, $C_{12}H_{15}NO_3$, and when this is heated with *opianic acid*, an oxidation product from meconine, $(CH_3O)_2C_6H_4(CHOH)(CO_2H)$, and H_2SO_4, *isonarcotine* is formed. This melts at 194° C. and is coloured red by strong H_2SO_4. From these reactions it is concluded that narcotine is a *meconinehydrocotarnine*.

Thebaine, $C_{17}H_{15}(OCH_3)_2NO$, is contained in opium in small proportion; it remains in the solution from which the hydrochlorides of morphine and codeine have crystallised. This solution is mixed with ammonia, which precipitates thebaine together with some narcotine; the precipitate is dissolved in a little acetic acid, and the narcotine precipitated by tribasic lead acetate. The lead is precipitated from the filtrate by dilute sulphuric acid, after which ammonia is added to precipitate the thebaine. This alkaloid, like morphine, is insoluble in water, but dissolves in alcohol and ether, and crystallises in plates; m.-p. 193° C. It is insoluble in alkalies. Its alcoholic solution is alkaline. Thebaine gives

a blood-red solution with strong sulphuric acid. When heated with hydrochloric acid, it yields an isomeride, *thebenine*, which gives a blue colour with sulphuric acid. Thebaine is very poisonous, producing tetanic convulsions.

Narceine, $C_{23}H_{27}NO_8$, remains in the solution from which the thebaine and narcotine have been precipitated by NH_3. This is mixed with lead acetate, to precipitate the rest of the narcotine, filtered, the lead removed by H_2SO_4, the filtrate neutralised by NH_3, and evaporated, when the narceine crystallises, leaving meconine in solution, which may be extracted by shaking with ether. Narceine crystallises from water in prisms with 3Aq; it is soluble in alcohol, but not in ether. It is a narcotic poison. Iodine colours its solution blue. It is also formed by heating narcotine methoiodide with KOH solution.

Papaverine, or *tetramethoxybenzylisoquinoline*, $(CH_3O)_2C_9H_4N{\cdot}CH_2C_6H_3(OCH_3)_2$, is contained, in small proportion, in the precipitate produced by excess of KOH in the aqueous solution of opium. The precipitate is dissolved in ether, and shaken with dilute acetic acid; the lower layer then contains the acetate of narcotine, thebaine, and papaverine; these are again precipitated by KOH and treated with oxalic acid, which leaves the acid papaverine oxalate undissolved. Papaverine is sparingly soluble in water, but dissolves in hot alcohol and ether. It gives a violet-blue solution with strong H_2SO_4. Its poisonous properties appear to be feeble. It melts at 148° C.

588. **Cinchona-alkaloids.**—The plants of the natural order *Cinchonaceæ* are remarkable for their medicinal properties. Conspicuous among them are *cinchona*, which furnishes quinine; the *coffee-tree*, which yields caffeine; and the *ipecacuanha*, which produces emetine.

Cinchona, or *Peruvian bark*, is obtained chiefly from the districts around the Andes, and owes its valuable febrifuge qualities to the presence of certain alkaloids, of which the most important are—

Quinine . . .	$C_{20}H_{24}N_2O_2$	Cinchonine . .	$C_{19}H_{22}N_2O$
Conquinine . .	$C_{20}H_{24}N_2O_2$	Cinchonidine . .	$C_{19}H_{22}N_2O$
Quinamine . .	$C_{19}H_{24}N_2O_2$		

Of these, quinine and cinchonine are by far the most important. The different species of cinchona yield a bark containing these alkaloids in different proportions. The *yellow* bark yields from 2 to 3 per cent. of quinine, and only 0.2 or 0.3 of cinchonine; the *red* bark, about 2 per cent. of quinine and 1 per cent. of cinchonine; and the *pale* or *grey* bark about 0.8 per cent. of quinine and 2 per cent. of cinchonine. The alkaloids exist in combination with quinic acid and with a variety of tannin known as quinotannic acid.

Quinine, $C_{20}H_{24}N_2O_2$, is prepared by boiling the bruised bark with diluted hydrochloric acid, and mixing the filtered solution with lime diffused through water, until it is alkaline. The precipitate, containing quinine, cinchonine, and colouring-matter, is filtered off and boiled with alcohol, which dissolves both the alkaloids, leaving the excess of lime undissolved. A part of the alcohol is then recovered by distillation, and the solution neutralised with sulphuric acid, boiled with animal charcoal till decolorised, and filtered. On standing, quinine sulphate crystallises out, leaving the cinchonine sulphate in solution. The quinine sulphate is dissolved in water, and decomposed by ammonia, which precipitates the quinine.

Quinine crystallises in prisms containing 3Aq, which dissolve in 1900 parts of cold water and easily in alcohol, ether, and chloroform; when anhydrous it melts at 117° C. Its solutions are alkaline, and bitter. It appears to be a tertiary di-amine, because, when heated with the iodides of alcohol radicles, it yields iodides which furnish ammonium bases when decomposed by AgOH; thus, methyl iodide gives $C_{20}H_{24}N_2O_2{\cdot}CH_3I$, which yields the alkaline hydroxide,

$$C_{20}H_{24}N_2O_2{\cdot}CH_3{\cdot}OH.$$

Quinine is characterised by exhibiting a beautiful blue *fluorescence* when dissolved in dilute sulphuric acid, and by producing a fine green colour when its dilute acid solutions are mixed with a little chlorine- or bromine- or euchlorine-water (see p. 779), and afterwards with ammonia. The green colour is due to the *thalleiochin*, formed by the reaction—

$$C_{20}H_{24}N_2O_2 + NH_3 + O_4 = C_{20}H_{27}N_3O_6.$$

Quinine is a di-acid base, but it sometimes forms salts in which it is monacid; there are two hydrochlorides; $C_{20}H_{24}N_2O_2.2HCl$ is converted by water into $C_{20}H_{24}N_2O_2.HCl$, which crystallises in needles of the formula $2(C_{20}H_{24}N_2O_2.HCl).3Aq$.

Normal quinine sulphate, $C_{20}H_{24}N_2O_2.H_2SO_4.7Aq$, is soluble in 11 parts of cold water, but the *basic sulphate*, $(C_{20}H_{24}N_2O_2)_2.H_2SO_4.8Aq$, requires 780 parts of cold water to dissolve it. This is the quinine salt generally used in medicine; it forms very light silky needles, which dissolve easily in dilute sulphuric acid, forming the *acid sulphate*, $C_{20}H_{24}N_2O_2.(H_2SO_4)_2.7Aq$, which is very soluble.

Quinine is very slightly soluble in potash, and sparingly in ammonia, though it is more soluble in NH_3 than is any other cinchona alkaloid. If normal quinine sulphate be dissolved in strong acetic acid, warmed, and an alcoholic solution of iodine added gradually, thin rectangular plates are deposited on cooling, having the formula $(C_{20}H_{24}N_2O_2)_4.(H_2SO_4)_3.(HI)_2.I_4.6H_2O$. These crystals (*herapathite*, or *artificial tourmaline*) are bronze green by reflection, but transmit light of a pale olive colour, which is perfectly polarised, like that transmitted by tourmaline, so that, if another plate be laid upon the first, no light is transmitted when their principal axes are at right angles.

Quinidine, or *conquinine*, $C_{20}H_{24}N_2O_2$, is isomeric with quinine, and is extracted from a brown substance called *quinoidine*, or *amorphous quinine*, which is obtained from the mother-liquors of quinine sulphate and is sold as a cheap substitute for quinine. It is also obtained in quantity from some of the inferior varieties of cinchona, such as *Cinchona cordifolia*, which yields the Carthagena bark. Quinidine forms larger prismatic crystals than quinine, and these contain only 2Aq. Its salts are more soluble than those of quinine, and they are strongly dextro-rotatory for polarised light, whilst those of quinine are lævo-rotatory.

Quinicine, also isomeric with quinine, is formed by heating quinine or quinidine with dilute sulphuric acid to 130° C. It is resinous, but its salts crystallise. Its solutions are feebly dextro-rotatory.

Cinchonine, $C_{19}H_{22}N_2O$, remains as sulphate in the mother-liquor from quinine sulphate (*v.s.*), and may be precipitated by ammonia. It is almost insoluble in water, and sparingly soluble in alcohol. Ether scarcely dissolves it, and is used to distinguish it from quinine. It crystallises from hot alcohol in anhydrous prisms, which have an alkaline reaction. It melts at 225° C. and sublimes in hydrogen. The salts of cinchonine are more soluble than those of quinine, and give a much more voluminous precipitate with ammonia, which is insoluble in a large excess, and is not cleared up by shaking with ether, as in the case of quinine.

Cinchonine sulphate, $(C_{19}H_{22}N_2O)_2.H_2SO_4.2Aq$, fuses when heated, evolving an aromatic odour and becoming red. Solution of cinchonine sulphate is less strongly fluorescent than one of quinine sulphate. Cinchonine also differs from quinine in yielding solutions which are strongly dextro-rotatory.

Cinchonidine is isomeric with cinchonine, but is strongly lævo-rotatory.

Cinchonicine, another isomeride, resembles quinicine in origin and properties.

When quinine, cinchonine, and their isomerides are fused with KOH, they yield the *quinoline bases*, indicating that they are closely connected with quinoline. The tarry odour on heating cinchonine is probably due to these. Thus both cinchonine and quinine are supposed to contain the quinoline group, the former being $C_9H_6N.C_{10}H_{13}(OH)N$, and the latter $(CH_3O)C_9H_5N.C_{10}H_{15}(OH)N$.

Emetine, $C_{30}H_{40}N_2O_8$, is a little-known base extracted from the root of *Cephaëlis ipecacuanha*, a cinchonaceous plant much used in medicine.

589. **Strychnos-alkaloids.**—Strychnine and brucine are obtained from *nux-vomica*, the seeds of the tropical plant, *Strychnos nux-vomica*, from *false angostura bark*,* which is the bark of the same tree, and from

* True angostura bark is obtained from *Galipea officinalis* and *G. cusparia*, belonging to the order Rutaceæ. It is used as a febrifuge.

Ignatia amara, or *St. Ignatius' bean*. Nux-vomica, or *crow-fig*, contains about 1 per cent. of strychnine and 1 per cent. of brucine.

Strychnine, $C_{21}H_{22}N_2O_2$, is extracted from the crushed seeds of nux-vomica by boiling them with very dilute HCl. The solution is mixed with milk of lime, and the precipitate filtered off and boiled with alcohol, which dissolves the strychnine and brucine, and deposits the strychnine first when evaporated. The mother-liquor is neutralised with HNO_3, when strychnine nitrate crystallises out, leaving brucine nitrate in solution. Both alkaloids are lævo-rotatory.

Strychnine crystallises in rhombic prisms, soluble in 7000 parts of water, and melting at 284° C. It is insoluble in ether and in absolute alcohol, but dissolves in dilute alcohol. It is very soluble in chloroform, which is the best agent for collecting it from aqueous solutions. Its intensely bitter taste is very remarkable, and may be imparted to one million parts of water (one grain in fourteen gallons). Its alcoholic solution is alkaline, and it is a monacid tertiary base, combining with methyl iodide to form *strychnine-methylium iodide*, $N_2C_{21}H_{22}O_2.CH_3I$, which yields the corresponding hydroxide base when decomposed by AgOH. But this ammonium base is not bitter, nor poisonous unless injected under the skin, when it induces paralysis. Strychnine is extremely poisonous, giving rise to tetanic convulsions. Potash precipitates strychnine from its solution in acids, and an excess does not dissolve it; the precipitate by ammonia dissolves in excess, but the strychnine crystallises out after a time. The smallest particle of strychnine may be identified by dissolving it in strong sulphuric acid and adding a minute fragment of potassium bichromate, which produces a fugitive blue-violet colour.

When strychnine is warmed with dilute HNO_3, it gives a faint pink solution, which becomes scarlet on adding a particle of powdered $KClO_3$; NH_3 changes this to brown, and, on evaporating to dryness, the residue is green and dissolves in water to a green solution, changed to orange by KOH, and becoming green again with HNO_3. Euchlorine-water (p. 779), or bromine-water, added to a solution of strychnine in HCl, gives, on boiling, a fine red colour, bleached by excess, and returning when boiled.

One of the N-atoms in strychnine is the tertiary ammonia nitrogen; the other appears to be in the form of a lactam group (p. 674) which becomes .

yielding *strychnic acid*, when strychnine is heated with sodium ethoxide. When the methylium iodide (*see above*) is treated with AgOH, the grouping

becomes .

Brucine, $C_{23}H_{26}N_2O_4$, is precipitated by KOH from the solution of brucine nitrate obtained in the extraction of strychnine. It is more soluble in water and alcohol than strychnine is, and crystallises in prisms with 4Aq. melting at 178° C. when anhydrous. Like strychnine, it is nearly insoluble in ether. It is intensely bitter and strongly basic. HNO_3 dissolves it with a fine red colour, which becomes violet on adding stannous chloride. Both strychnine and brucine yield quinoline bases when distilled with KOH; indicating their relationship with quinoline. The proportion of methyl alcohol obtainable from brucine by distilling it with MnO_2

and H_2SO_4 shows that it contains $2(OCH_3)$; it may, therefore, be regarded as dimethoxy-strychnine.

590. **Aconitine**, $C_{33}H_{43}NO_{12}$, is extracted from the root of *Aconitum napellus*, a plant of the Ranunculaceous or Buttercup order, known as *monk's hood*, *blue rocket*, and *wolf's bane*. The root has often been scraped and eaten by mistake for *horse-radish* (*Cochlearia armoracia*, a cruciferous plant), but the two roots are really very unlike, and the scrapings of monk's hood become pink when exposed to air, while those of horse-radish remain white. To extract the aconitine, the scrapings of the root are boiled with amyl alcohol; the solution is shaken with dil. H_2SO_4, which extracts the aconitine, and the aqueous liquid is neutralised with Na_2CO_3. The aconitine thus precipitated is crystallised from ether. It crystallises from alcohol in anhydrous plates (m.-p. 188° C.), and forms well-defined salts. Aconitine is one of the most poisonous alkaloids, and, as yet, no trustworthy chemical test for it is known, so that the toxicologist is obliged to place a little of the suspected substance on the tongue, when aconotine produces a numbing, tingling feeling, lasting for some time. When heated with potash, aconitine yields potassium benzoate and *aconine*, $C_{25}H_{41}NO_{11}$. The preparations sold as aconitine are often impure bases of very variable quality.

Pseudaconitine, $C_{36}H_{49}NO_{12} + H_2O$, is a poisonous alkaloid obtained from *Aconitum ferox*, an Indian plant of the same natural order. Heated with potash, it yields *pseudaconine*, $C_{27}H_{41}NO_9$, and the potassium salt of dimethyl dihydroxybenzoic (or dimethyl protocatechuic) acid.

Veratrine, $C_{37}H_{53}NO_{11}$, is extracted from the root of white hellebore (*Veratrum album*), and from the seeds of *Veratrum sabadilla*, plants of the natural order Colchicaceæ. The alkaloid is present in very minute quantity. It is extracted by digesting the root with alcohol containing a little tartaric acid, evaporating the alcohol from the filtered solution, dissolving the residue in water, liberating the alkaloid by caustic soda, and shaking with ether, which dissolves it. The ethereal layer leaves the alkaloid when evaporated. Veratrine is characterised by its power to cause violent sneezing when a particle of the powder is drawn into the nose. It dissolves in HCl, and the solution becomes red when gently heated. Strong H_2SO_4 gives a yellow solution passing into carmine-red, and becoming purple with bromine-water. *Ceradine*, $C_{32}H_{49}NO_9$, is another alkaloid which causes sneezing, and is extracted from Cevadilla seeds (*Veratrum sabadilla*). *Veratralbine*, $C_{29}H_{43}NO_5$; *jervine*, $C_{26}H_{37}NO_3$; *pseudojerrine*, $C_{29}H_{43}NO_7$; and *rubijerrine*, $C_{26}H_{43}NO_3$, are also extracted from the Veratrums. These plants are chiefly used for poisoning vermin.

Bebeerine, $C_{19}H_{21}NO_3$, is extracted from the bark of the bibiru-tree, a tree of the Laurel order, which grows in British Guiana, and yields the *green-heart* wood used in shipbuilding, because it resists the attacks of marine animals. It is amorphous, insoluble in water, but soluble in alcohol. The sulphate, $(C_{19}H_{21}NO_3)_2.H_2SO_4$, is sometimes used in medicine instead of quinine sulphate.

Berberine, $C_{20}H_{17}NO_4$, is obtained from the root of the barberry (*Berberis vulgaris*), and from calumba-root (*Cocculus palmatus*) and false calumba-root (*Menispermum fenestratum*), both belonging to the Menispermaceæ. Berberine crystallises in yellow needles with $5\frac{1}{2}$Aq, and forms yellow salts. It is soluble in water.

591. *Hydrastin*, $C_{21}H_{21}NO_6$, (m.-p. 132° C.) is an alkaloid of constitution similar to that of narcotine also obtained from barberry.

Physostigmine, or *eserine*, $C_{15}H_{21}N_3O_2$, is obtained from the Calabar bean, the seed of a Papilionaceous plant. It is sparingly soluble in water, but dissolves in alcohol, is strongly alkaline, and very poisonous. It has the property of contracting the pupil of the eye.

Colchicine, $C_{22}H_{25}NO_6$, occurs in meadow saffron, *Colchicum autumnale* (belonging to the same order as the Veratrums); much used as a remedy in gout. It is a very feeble base, soluble in water and alcohol, and does not crystallise.

Cytisine, $C_{11}H_{14}N_2O$, is the poisonous alkaloid contained in the seeds of *Cytisus laburnum*, a Papilionaceous plant.

Chelidonine, $C_{20}H_{19}NO_5$, has been extracted from celandine (*Chelidonium majus*), a plant of the Poppy order.

Delphinine, $C_{22}H_{35}NO_6$, is the poisonous alkaloid contained in larkspur or staves-acre (*Delphinium staphisagria*), the seeds of which are used for destroying vermin (aconite belongs to the same order).

Pilocarpine, $C_{11}H_{16}N_2O_2$, is extracted from the leaves of *Pilocarpius pennatifolius*,

a plant of the Rue order. The base itself is not crystalline, but the hydrochloride and nitrate are crystalline salts, which are used in medicine.

Jaborandine, $C_{10}H_{12}N_2O_3$, is another alkaloid obtained from the same source.

PHYSICAL PROPERTIES OF ORGANIC COMPOUNDS.

592. In investigating the chemical structure of the molecules of organic bodies, much assistance is derived from the observation of their physical properties, among which the following are the most important:—

(1) The *fusing-point* of a solid, the *boiling-point* of a liquid, and the *specific gravity* of a vapour.

(2) The *specific volume* of a liquid, obtained by dividing its molecular weight by its specific gravity (calculated for the temperature at which the liquid boils).

(3) The *optical properties* of a liquid, or of a solid body in solution; especially the *action on polarised light*, the *refractive power*, the *absorption spectrum*, and the *magnetic rotatory power* deduced from its action on a ray of polarised light when under the influence of magnetism.

593. **Fusing-points of organic compounds.**—In order that a solid may fuse, it must first attain to a degree of temperature called the *fusing-point* of the solid, and must then have a certain amount of motion imparted to its molecules by the transformation (into motion) of an amount of heat which is termed *latent heat* or *heat of fusion*. This motion enables the molecules to circulate more or less freely among themselves, and to extend themselves in a horizontal plane.

The fusing-point, as indicated by the thermometer, therefore, is the temperature at which the molecules become capable of converting the heat subsequently acquired into the motion proper to the liquid condition. This temperature will depend upon the constitution of the molecules, which regulates their relation to adjacent molecules.

If the *cohesion* which limits the motion of molecules in a solid mass be similar in character to the *gravitation* which limits the motion of masses of matter, it will be greater among those molecules which have the larger *mass*, that is, the highest molecular weight, and these should have the highest fusing-points, since a larger amount of progressive motion (or *temperature*) must be imparted to them to render them capable of acquiring the freedom of motion proper to the liquid condition. But it is by no means true that the fusing-point is always higher when the molecular weight is greater; for palmitin, with a molecular weight of 806, fuses at 63° C., while urea, with a molecular weight of 60, fuses at 130° C. It may be stated, however, that in the case of homologous series, the fusing-point generally rises as the molecular weight increases; thus the paraffin and olefine hydrocarbons are liquids until they contain sixteen atoms of carbon. The substitution of HO for H tends to raise the fusing-point, so that the paraffin alcohols containing more than seven carbon-atoms are solids, and this is also the case with the aldehydes.

In the case of the metameric paraffin derivatives the fusing-point is generally higher in those compounds which contain most carbon in the form of CH_3; thus, pseudo-valeric or tertiary valeric acid, $C(CH_3)_3 \cdot CO_2H$, fuses at about 35° C., while normal valeric acid, $CH_3[CH_2]_3 \cdot CO_2H$, fuses at −59° C. Again, tertiary butyl-alcohol, $C(CH_3)_3 \cdot OH$, fuses at 25° C.; and normal butyl-alcohol, $CH_3[CH_2]_3 \cdot OH$, is liquid even below 0° C.

In the benzene-hydrocarbons, the substitution of CH_3 for H raises the fusing-point: thus, toluene, $C_6H_5 \cdot CH_3$, and xylene, $C_6H_4(CH_3)_2$, are liquids; but durene, $C_6H_2(CH_3)_4$, fuses at 80° C. In these also, when they have the same molecular weight, the fusing-point rises with the number of methyl groups directly united to carbon; for example, amyl-toluene, $C_7H_7 \cdot [CH_2]_4 \cdot CH_3$, is liquid, while hexamethyl-benzene, $C_6(CH_3)_6$, is solid, fusing at 164° C. Even in compounds which are strictly isomeric, the position of the component radicles will affect the fusing-point, the para-compound having generally the highest fusing-point; thus, ortho-xylene and meta-xylene are liquids, but para-xylene is a solid fusing at 15° C.

594. **Boiling-points of organic compounds.**—The boiling-point of a liquid is that temperature at which its molecules are capable of converting heat into motion sufficient to enable them to overcome entirely the attraction holding them to each other, and to extend themselves in all directions through space. Under ordinary conditions, their extension is impeded by the pressure of the atmosphere upon the surface of the liquid, so that, for experimental work, the boiling-point is that temperature at which the molecules are capable of acquiring sufficient motion to overcome a pressure of 760 millimetres of mercury (at 0° C.). Since the boiling-point refers to a certain standard of external work, it exhibits a more definite relation to the constitution of the molecules than is the case with the fusing-point. In homologous series, the boiling-point increases with the molecular weight, but the increase due to each addition of CH_2 varies in different series. It is most uniform in the normal primary alcohols of the paraffin series (p. 565), where each addition of CH_2 increases the boiling-point, on the average, by 19.5° C. In the series of aldehydes derived from these alcohols (p. 583), the increase in boiling-point is also fairly regular, but it averages 26.2° for each addition of CH_2. In the corresponding acids, the increase is much less uniform, but the average increase is about 19°. In the single ketones (p. 624), the mean increase in boiling-point for each CH_2 added is 20.5°. In the simple ethers, the increase is 26°.

In the homologous series of hydrocarbons, the increase in boiling-point for each addition of CH_2 is irregular, but generally diminishes as the number of carbon-atoms increases. Those hydrocarbons of the paraffin and olefine series which contain the same number of carbon-atoms exhibit a similarity in their boiling-points :—

Paraffins	C_5H_{12} 37°	C_6H_{14} 69°	C_7H_{16} 98°	C_8H_{18} 125°	$C_{16}H_{34}$ 288°
Olefines	C_5H_{10} 35°	C_6H_{12} 69°	C_7H_{14} 99°	C_8H_{16} 123°	$C_{16}H_{32}$ 275°

The isologous hydrocarbons of the acetylene series have higher boiling-points, and those of the benzenes are higher still—

Acetylenes	C_5H_8 45°	C_6H_{10} 80°	C_7H_{12} 106°	C_8H_{14} 133°	$C_{10}H_{18}$ 165°
Benzenes	...	C_6H_6 80·1°	C_7H_8 111°	C_8H_{10} 142°	$C_{10}H_{14}$ 196°

The substitution of HO for H in the conversion of the paraffin hydrocarbons into alcohols increases the boiling-point greatly, but in a ratio which decreases in nearly the same proportion in which the molecular weight of the alcohol increases—

Hydrocarbons	C_5H_{12} 37°	C_6H_{14} 69°	C_7H_{16} 98°	C_8H_{18} 125°
Alcohols . .	$C_5H_{12}O$ 137°	$C_6H_{14}O$ 157°	$C_7H_{16}O$ 170°	$C_8H_{18}O$ 191°

A similar increase in boiling-point is produced by the substitution of HO for H in the conversion of an aldehyde into an acid—

Aldehydes	C_2H_4O 20.8°	C_3H_6O 48°	C_4H_8O 74°	$C_5H_{10}O$ 103°
Acids .	$C_2H_4O_2$ 118·3°	$C_3H_6O_2$ 140.7°	$C_4H_8O_2$ 162°	$C_5H_{10}O_2$ 186°

Metameric bodies which belong to the same class often have nearly the same boiling-points—*e.g.*, propione, $C_2H_5{\cdot}CO{\cdot}C_2H_5$ 101° ; methyl-propyl ketone, $CH_3{\cdot}CO{\cdot}C_3H_7$ 102°.

But this is not the case when they belong to different classes—*e.g.*, methyl-ethyl ketone, $CH_3{\cdot}CO{\cdot}C_2H_5$ 81° ; methyl-allyl ether, $CH_3{\cdot}O{\cdot}C_3H_5$ 46°.

The ethereal salts have lower boiling-points than the acids which are metameric with them—*e.g.*, methyl formate, $CH_3{\cdot}CHO_2$ 36° ; acetic acid, $H{\cdot}C_2H_3O_2$ 118°.

In the isomeric hydrocarbons, the normal compound has the highest boiling-point, which falls as the number of methyl groups increases : thus, normal butane, $H_3C[CH_2]_2CH_3$, is liquefied at 1° C., while iso-butane, $H_3C{\cdot}CH(CH_3){\cdot}CH_3$, remains gaseous till − 17° C.

The boiling-point is lowered, in these isomeric hydrocarbons, by the substitution of ethyl and methyl for hydrogen, and is lowest in those compounds in which the carbon is united to the compound radicles only. The same tendency is observed in the isomeric olefines ; thus amylene, $H_3C[CH_2]_2CH : CH_2$, boils at 73°, and iso-amylene, $(H_3C)_2C : CH(CH_3)$ at 35°.

The normal primary alcohols have the highest boiling-points, then come the iso-alcohols, while the secondary and tertiary alcohols have the lowest boiling-points. The same may be said of the aldehydes and acids.

When any other element or group is substituted for hydrogen in an organic compound, the boiling-point is raised, and if more than one atom of hydrogen be displaced, the boiling-point, in the isomerides thus produced will generally

be higher where the substituting radicles are at the greatest distance from each other. Thus, ethylidene dichloride, $H_3C{\cdot}CHCl_2$, boils at 58° ; whilst ethene dichloride, $ClH_2C{\cdot}CH_2Cl$, does not boil till 85°. Again, dibromopropane, $H_3C{\cdot}CBr_2{\cdot}CH_3$, boils at 114° ; propene dibromide, $H_3C{\cdot}CHBr{\cdot}CH_2Br$, at 142° ; and trimethene dibromide, $BrH_2C{\cdot}CH_2{\cdot}CH_2Br$, at above 160°. Ortho-cresol, $C_6H_4CH_3{\cdot}OH$ (1 : 2), boils at 190° ; meta-cresol (1 : 3) at 195° ; and para-cresol (1 : 4) at 198°. Ortho-chloraniline, $C_6H_4Cl{\cdot}NH_2$ (1 : 2), boils at 207° ; meta-chloraniline (1 : 3) at 230° ; and para-chloraniline (1 : 4) at 231°. Diamidotoluene, $C_6H_3(CH_3)(NH_2)_2$ (1 : 2 : 3), boils at 270° ; and (1 : 2 : 4) at 280°. Further investigation of the boiling-points of isomerides is necessary fully to establish this law.

595. **Specific volumes of organic liquids.**—It has been seen that the specific volumes of the *vapours* of organic compounds, obtained by dividing the molecular weight by the vapour-density, are in all cases alike ; but this is not the case with the specific volumes of *liquids*, which depend upon the attraction exerted between their molecules, which must of course vary with the nature of the molecules themselves. Since, at their respective boiling-points, all liquids are in a similar condition in regard to the further effect of heat upon them, it might be expected that their molecular weights, divided by their specific gravities (at the boiling-point), would yield quotients bearing some definite relation to each other, since these quotients represent the *molecular volumes* of the compounds in the liquid state (at the boiling-point) ; that is, the relative (or specific) volumes within which the motions of each molecule are restricted, or the space in which each molecule keeps free from other molecules.

The molecular volume of water, calculated in this way, is 18·8 ; that of methyl alcohol is 42. Then $CH_4O - H_2O = CH_2$; and $42 - 18.8 = 23.2$, which is the increase in molecular volume, due to the addition of CH_2 to H_2O. The molecular volume of ethyl-alcohol is 62.5, or higher than that of methyl-alcohol by 20.5, which represents the increase due to CH_2. The molecular volume of acetic acid is 64, and that of formic acid 42, giving 22 as the increase due to CH_2. The mean of the three values is 21.9, and this is almost exactly the difference in the molecular volumes calculated for the homologous acids, from formic to valeric.

At one time it was stated with confidence that the molecular volume depends on the number and nature of the atoms contained in the molecule rather than on their grouping ; thus, ethyl acetate, $CH_3{\cdot}COOC_2H_5$, has the same molecular volume as its metameride, butyric acid, $C_3H_7{\cdot}COOH$. Recently, much doubt has been cast on this statement ; and it has been asserted that, instead of the molecular volume being the sum of the atomic volumes, it depends on the manner in which the atoms are united. The following is the evidence in favour of the older view.

Octane, C_8H_{18}, has a molecular volume = 187, and if we deduct from this $(CH_2)_8 = 176$, the difference, 11, represents the molecular volume of H_2, giving 5·5 for the *atomic volume* of hydrogen. Cymene, $C_{10}H_{14}$, has the molecular volume 187, which differs from $(CH_2)_7$, or 22×7, by 33, which represents the increase in molecular volume due to C_3, and gives 11 for the atomic volume of carbon.

By deducting the volume of H_2 (11) from that of H_2O (18.8), 7.8 is obtained for the atomic volume of oxygen.

From these values the specific volumes of many molecules may be calculated and are found to agree very nearly ; with those obtained by dividing the molecular weight by the specific gravity of the liquid at its boiling-point ; for example—

Methyl alcohol, CH_4O, gives		$11 + (5.5 \times 4) + 7.8 = 40.8$	instead of	42
Ethyl	„	C_2H_6O „	$(11 \times 2) + (5.5 \times 6) + 7.8 = 62.8$	„	62.5
Ether	„	$C_4H_{10}O$ „	$(11 \times 4) + (5.5 \times 10) + 7.8 = 106.8$, which is correct.		
Phenol	„	C_6H_6O „	$(11 \times 6) + (5.5 \times 6) + 7.8 = 106.8$	„	„

But formic acid, CH_2O_2, the specific volume of which is 41.5, gives only 37.6 as the sum of $11 + (5.5 \times 2) + (7.8 \times 2)$.

Again, acetone, C_3H_6O, with a specific volume = 77.6, gives only 73.8 (which agrees with that found for allyl-alcohol, also C_3H_6O) by the addition of

$$(11 \times 3) + (5.5 \times 6) + 7.8$$

The structural formula of acetone is $(CH_3)_2{\cdot}C{:}\,O$, the oxygen being doubly linked to a carbon atom, whilst in the alcohols, ethers, and phenols it is only singly linked to a carbon atom.

Deducting from the specific volume of acetone (77.6) that of C_3H_6 (66), there remains 11.6 as the atomic volume of oxygen, when doubly linked to a carbon atom.

Formic acid contains a singly linked and a doubly linked oxygen atom ; hence its molecular volume should be the sum of $11+(5.5\times2)+7.8+11.6=41.4$, which is very nearly correct.

Acetic acid, $H_3C(C:O)OH$, gives $(5.5\times4)+(11\times2)+7.8+11.6=63.4$, instead of 63.6.

Aldehyde, $H_3C(C:O)H$, gives $22+22+11.6=55.6$, instead of 56.5, whereas if its formula were $H_2C{\cdot}O{\cdot}CH_2$, it would give $22+22+7.8=51.8$.

The specific volume of an atom of nitrogen singly linked to carbon, as in methylamine, $H_3C{-}NH_2$, is 2.3 ; but when trebly linked to carbon, as in methyl cyanide, $H_3C{-}C{\equiv}N$, its specific volume is 17.

Sulphur, singly linked to carbon, has the specific volume 23 ; but when doubly linked, it is 28.6. The specific volume of chlorine is 22.8, of bromine 27.8, and of iodine 37.5

There are many exceptions to the simple laws of specific volume here set forth. Thus, ethylene chloride, $ClH_2C.CH_2Cl$, and ethylidene chloride, $H_3C{\cdot}CHCl_2$, which have the calculated specific volume 89.5, give, by experiment, respectively, 85.34 and 88.96, a difference too great to be ascribed to experimental errors. Benzene, and some other members of the aromatic group, also exhibit considerable deviation, the observed specific volumes being lower than those calculated.

596. **Optical properties of organic compounds.**—Since the phenomena of light depend upon the waves excited in the æther which fills the spaces between the molecules of matter, the motions of these molecules must exert an influence upon the optical properties of the substances which they compose.

The molecular conditions which regulate the *colour* of compounds, by enabling them to absorb certain of the waves composing white light, and to reflect or transmit others, are not as yet understood, but colour is most commonly associated with high molecular weight. (See also *Quinonoid structure*, p. 721.)

Much attention has been devoted to the comparison of the *refractive powers* of liquid organic compounds, that is, to the amount of deviation from its original path which a wave of light suffers in passing through the liquid in any direction except that perpendicular to the surface. The full discussion of this subject requires the study of optics, but it may be stated that from the amount of deviation is calculated the *specific refractive power* of the liquid, which is closely connected with the nature of its molecules. The *molecular refractive energy*, or *refraction-equivalent*, is found by multiplying the molecular weight by the specific refractive power. Compounds which have the same molecular weight and belong to the same or to nearly related classes of organic compounds, generally have nearly the same refraction-equivalent; thus, the number for methyl acetate, $CH_3{\cdot}C_2H_3O_2$, is 28.78 and that for ethyl formate, $C_2H_5{\cdot}CHO_2$, is 28.61. Butylalcohol, $C_4H_9{\cdot}OH$, gives 36.11, and ether, $C_2H_5{\cdot}O{\cdot}C_2H_5$, 36.26. Polymeric bodies have refraction-equivalents nearly proportionate to their molecular weights ; thus, aldehyde, C_2H_4O, has the refraction-equivalent 18.5, butyric acid, $C_4H_8O_2$, 36.6, and paraldehyde, $C_6H_{12}O_3$, 52.5. In the homologous alcohols and acids derived from the paraffin hydrocarbons, the refraction-equivalent increases by about 7.6 for each addition of CH_2 ; thus, acetic acid, $C_2H_4O_2$, having the refraction-equivalent 21.1, œnanthic acid should give $21.11+(7.6\times5)=59.1$, which nearly agrees with that observed, 59.4.

By a method similar to that explained in the case of specific volumes, the refraction-equivalents to the elements may be calculated, and they are found to be, for the wave-length corresponding with the yellow sodium line, for carbon 4.71, for hydrogen 1.47, for oxygen singly linked to carbon, 2.65, and for oxygen doubly linked, 3.33. From these numbers the refraction-equivalent of a liquid may be calculated from its formula, as in the case of its specific volume, and the result agrees very nearly, in a great many cases, with that obtained by experiment. But there is sufficient deviation to indicate that the grouping of the atoms, as well as their nature and number, influences the refraction-equivalent. Thus, in the terpenes, the observed equivalent exceeds that calculated by the constant number 3, while in the benzenes the excess amounts to 6. It would appear that when a carbon atom is doubly linked to another carbon atom, its refraction-equivalent is 5.71 instead of 4.71, so that the six doubly-linked carbon atoms in the benzene ring would explain the excess in the refraction-equivalent.

When liquids having different refraction-equivalents are mixed, the refraction-equivalent of the mixture is the sum of those of its constituents, so that the proportions in which these are present may be calculated.

The *rotation of the plane of polarised light* (p. 542) affords another optical method of investigating the constitution of organic substances.

The angle of rotation, in the case of any given substance, varies directly as the strength of the solution, its specific gravity, and the length of the column of liquid through which the light passes. For different substances, the angle of rotation also varies with the *specific rotatory power*, which is found by dividing the angle of rotation by the product obtained by multiplying together the weight of the substance in one gramme of the liquid, the specific gravity of the liquid, and the length of the column in decimetres. For example, a beam of polarised light was passed through a tube with glass ends, 0.50 decimetre long, filled with turpentine, of specific gravity (at the temperature of the experiment) 0.8712, and it was requisite to turn the analyser 16° in the opposite direction to the hand of a watch in order to prevent light from reaching the eye of the observer. This would give for the specific (lævo) rotatory power, $\frac{16}{1 \times 0.8712 \times 0.5} = 36.7$. It is evident that if the specific rotatory power of a substance be known, a calculation like this would give the weight contained in each gramme of the solution, and this is turned to account in the *saccharimeter* for determining the proportion of sugar in a solution.

This rotatory power is found most commonly in vegetable and animal products and their immediate derivatives, as will have been seen in the description of such bodies, and it has been pointed out that it depends upon some peculiarity in the structure of the molecule. Recent observations render it probable that much information will be derived from the study of circular polarisation with respect to the true configuration of molecules, as has been indicated at p. 605.

All liquids exhibit some rotatory power for polarised light when they are under the influence of a powerful (electro) magnet, and the amount of the rotation, compared with that produced by water under the same conditions, is called the *magnetic rotatory power*. The *molecular magnetic rotation* obtained by multiplying the rotatory power by the molecular weight, and dividing by the specific gravity of the liquid, exhibits a definite relation to the composition of the molecule, and increases by 1.023 for each addition of CH_2 in homologous series. Proceeding on the same principle as in the case of specific volumes (p. 786), the *atomic magnetic rotatory power* of carbon is found to be 0.515, that of hydrogen, 0.254, of singly linked oxygen, 0.194, and of doubly linked oxygen, 0.263, and from these, in many cases, the molecular magnetic rotatory power of compounds may be calculated, or conversely, a knowledge of the rotatory power may be applied to determine a molecular formula.

597. **Absorption spectra of organic compounds for chemical rays.**—The light emanating from the sun and from the electric spark is accompanied by many other waves whose period of vibration is so short that they produce no impression upon the eye, or upon the thermometer, and are only detected by their power of chemically decomposing the salts of silver and other photographic materials. The shortness of these waves causes them to suffer a greater amount of deviation or refraction than the luminous waves when the light is passed through a prism, so that their effects are chiefly perceived in that part of the spectrum which lies beyond the violet light, and is usually termed the *ultra-violet*. Many substances which are perfectly transparent are able to intercept a large proportion of these *actinic* waves, as they are termed, and are said to be *adiactinic*, whilst those which transmit them freely are *diactinic*.

Rock crystal, or quartz, is much more diactinic than glass, and lenses and prisms of this material are used in experiments upon this subject, the light of a stream of electric sparks being allowed to pass through the slit of a spectroscope (p. 328), through a cell with quartz sides containing the liquid under examination, then through a quartz lens and prisms and afterwards received upon a sensitive photographic plate upon which that portion of the ultra-violet waves which has passed through leaves its impression.

It has been shown, by such experiments, that the normal alcohols derived from the paraffins are highly diactinic, and that the corresponding acids are somewhat less so, absorbing more of the highly refrangible waves remote from the violet end of the spectrum; the diactinic character decreasing, in both acids and alcohols, as the molecular weight increases. Benzene and its derivatives are highly adiactinic,

and, when employed in strong solutions, are often capable of absorbing all the ultra-violet waves ; but when diluted to a certain extent with water or alcohol, they allow some of the waves to pass, and produce photographs of spectra exhibiting *absorption-bands* due to this *selective absorption*. Since isomeric benzene derivatives exhibit very different absorption-bands, the selective absorption must be due to vibrations within the molecules, while the general absorption, which varies with the molecular weight, is caused by the vibration of the molecules themselves. There is very strong evidence that the absorption-bands in the ultra-violet spectrum are exhibited only by those compounds in which the carbon atoms form *closed chains*, as in benzene (p. 542), and naphthalene (p. 552), in which there are three pairs of doubly linked carbon atoms.

Starch, glucose, saccharose, diastase, and gelatine are highly diactinic, and show no absorption-bands, while albumin, casein, and serin exhibit absorption-bands in dilute solution.

The photographic absorption-spectra afford a most accurate method of identifying organic substances, and a most delicate test of their purity, since the absorption-bands are visible in solutions of extreme dilution.

ON SOME OF THE

USEFUL APPLICATIONS OF THE PRINCIPLES OF ORGANIC CHEMISTRY.

DESTRUCTIVE DISTILLATION OF COAL.

598. An extraordinary progress has been made by chemistry since the introduction of the manufacture of coal-gas. No other branch of manufacture has brought into notice so many compounds not previously obtained from any other source, and above all, offering, at first sight, so very little promise of utility, as to press urgently upon the chemist the necessity for submitting them to investigation.

Although many important additions to chemical knowledge have resulted from the labours of those who have engaged in devising the best methods of obtaining the coal-gas itself in the state best fitted for consumption, far more benefit has accrued to the science from investigations into the nature of the secondary products of the manufacture, the removal of which was the object to be attained in the purification of the gas.

Of the compounds of carbon and hydrogen, very little was known previously to the introduction of coal-gas; and although the liquid hydrocarbons composing coal-naphtha were originally obtained from other sources, the investigation of their chemical properties has been greatly promoted by the facility with which they may be obtained in large quantities from that liquid. The most important of these hydrocarbons, *benzole* or *benzene*, was originally procured from benzoic acid; but it would have been impossible for it to have fulfilled its present useful purposes unless it had been obtained in abundance as a secondary product in the manufacture of coal-gas; for, leaving out of consideration the various uses to which benzene itself is devoted, it yields the *nitrobenzene* so much used in perfumery, and from this we obtain *aniline*, from which many of the most beautiful dyes have been prepared.

The *naphthalene* found so abundantly in coal-tar possesses a peculiar interest, as having formed the subject of the classical researches by which Laurent was led to propose the doctrine of substitution, which has since thrown so much light upon the constitution of organic substances.

We are also especially indebted to coal-tar for our acquaintance with the very interesting and rapidly extending class of volatile alkalies, of which the above-mentioned aniline is the chief representative, and for *phenic* or *carbolic acid*, from which are derived the large number of substances composing the phenyl series.

The retorts in which the distillation of coal is effected are made of fire-clay, generally having the form of a flattened cylinder, and arranged in sets of three or five, heated by the same coal-fire or gas furnace (Fig. 284). The coal is thrown on to the red-hot floor of the retort, as soon as the coke from the previous distillation has been raked out; the mouth of the retort is then closed with an iron plate luted with clay. An iron pipe rises from the upper side of the front of the retort projecting from the furnace, and is curved round at the upper extremity, which passes into the side of a much wider tube, *b*, called the *hydraulic main*, running above the furnaces, at right angles to the retorts, and receiving the tubes from all of them. This tube is always kept half full of the tar and water condensed from

the gas, and below the surface of this liquid the delivery tubes from the retorts are allowed to dip, so that, although the gas can bubble freely through the liquid, as it issues from the retort, none can return through the tube whilst the retort is open for the introduction of a fresh charge.

Exhausters are used in most gas-works, to prevent the pressure in the retort from exceeding that of the atmosphere, thus diminishing loss by leakage, and quickly removing the gas from the injurious effect of the hot retort.

The aqueous portion of the liquid deposited in the hydraulic main is known as the *ammoniacal liquor*, from its consisting chiefly of a solution of various salts of ammonium, the chief of which is the carbonate; sulphide, cyanide and sulphocyanide of ammonium are also found in it.

From the hydraulic main the gas passes into the *condenser*, *e*, which is composed of a series of bent iron tubes kept cool either by the large surface which they expose to the air, or sometimes by a stream of cold water. In these are deposited, in addition to water, any of the volatile hydrocarbons and ammonium salts which may have escaped condensation in the hydraulic main. Even in the condenser the removal of the ammoniacal salts is not complete, so that it is usually necessary to pass the gas through a *scrubber* or case containing fragments of coke, over which a stream of water is allowed to trickle, in order to absorb the remaining ammoniacal vapours.

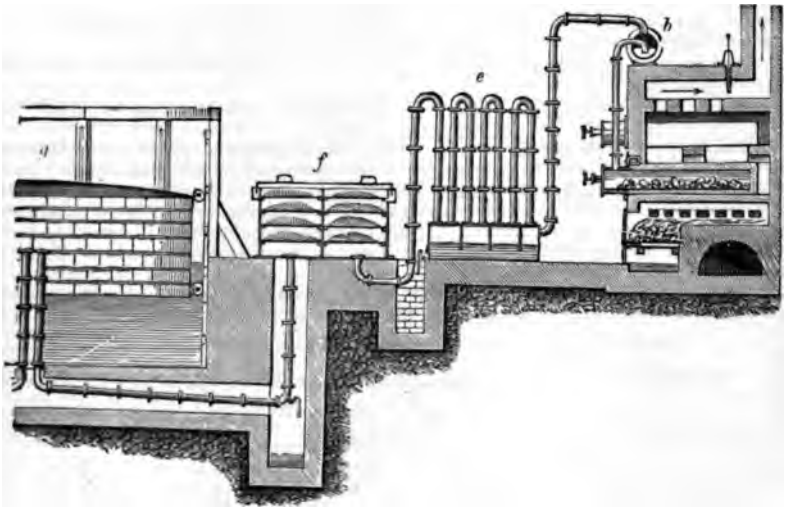


Fig. 284.—Manufacture of coal-gas.

The *tar* which condenses in the hydraulic main is a very complex mixture, of which the following are some of the leading components :—

Neutral Hydrocarbons.	Alkaline Products.
Liquid.	Ammonia.
Benzene	Aniline.
Toluene.	Picoline.
Xylene.	Quinoline.
Isocumene.	Pyridine.
Solid.	Acid Products.
Naphthalene.	Carbolic acid.
Anthracene.	Kresylic.
Chrysene.	Rosolic.
Pyrene.	Acetic.

The gas is now passed through the *lime-purifier*, *f*, which is an iron box with shelves on which dry slaked lime is placed in order to absorb the carbonic acid gas, sulphuretted hydrogen, and carbon bisulphide.

A great many other methods have been devised for the purification of the gas from sulphuretted hydrogen, but none appears to be so efficacious and economical as that which consists in passing the gas over hydrated iron oxide* mixed with sawdust (which is employed to prevent the material from caking).

The action of the sulphuretted hydrogen on the ferric oxide is represented by two equations (1) $Fe_2O_3 + H_2S = 2FeO + H_2O + S$; (2) $Fe_2O_3 + 3H_2S = 2FeS + 3H_2O + S$; and the circumstance which especially conduces to the economy of the process is the facility with which the ferrous sulphide and oxide may be reconverted into the ferric oxide by mere exposure to the action of atmospheric oxygen; for $2FeS + O_3 = Fe_2O_3 + S_2$, thus reviving the power of the mixture to absorb sulphuretted hydrogen. Accordingly, the material is periodically exposed to the action of air; or, as is sometimes practised, a small quantity of air is admitted into the purifier together with the gas; this reconverts the ferrous sulphide and oxide into ferric oxide, and the oxidation is attended with enough heat to convert into vapour any benzene which may have condensed in the purifying mixture, and of which the illuminating value would otherwise be lost. The same purifying mixture may thus be employed to purify a very large quantity of gas, until the separated sulphur (55 per cent.) has increased its bulk to an inconvenient extent, when the *spent oxide* is burnt for making vitriol (p. 225). The process for removing the carbon bisulphide vapour is mentioned at p. 241.

The purified gas is passed into the gasometer, *g*, from which it is supplied for consumption.

In the manufacture of coal-gas, attention is requisite to the temperature (1800° to 2000° F.), at which the distillation is effected, for, if it be too low, the solid and liquid hydrocarbons will be formed in too great abundance, not only diminishing the volume of the gas, but causing much inconvenience by obstructing the pipes. On the other hand, if the retort be too strongly heated, the vapours of volatile hydrocarbons, as well as the olefiant gas and marsh gas, may undergo decomposition, depositing their carbon upon the sides of the retort, in the form of *gas-carbon*, and leaving their hydrogen to increase the volume and dilute the illuminating power of the gas.

These effects are well exemplified in the following table, which contains analyses of the gas collected at different periods of the distillation:—

In 100 volumes.	After 10 mins.	After 1½ hours.	After 3½ hours.	After 5½ hours.
Sulphuretted hydrogen	1.30	1.42	0.49	0.11
Carbon dioxide	2.21	2.09	1.49	1.50
Hydrogen	20.10	38.33	52.68	67.12
Carbon monoxide	6.19	5.68	6.21	6.12
Marsh gas	57.38	44.03	33.54	22.58
Illuminants (see p. 161)	10.62	5.98	3.04	1.79
Nitrogen	2.20	2.47	2.55	0.78

Much advantage is said to be gained by mixing the coal with a certain proportion of lime, which diminishes the sulphur in the gas and increases the yield of ammonia.

One of the most useful of the secondary products of the coal-gas manufacture is the ammonia, and this process has been already noticed as a principal source of the ammoniacal salts found in commerce.

Next in the order of usefulness stands the coal-tar, which deserves attentive consideration, not only on that account, but because the extraction of the various useful substances from this complex mixture affords an excellent example of

* Brown hæmatite (bog ore) is frequently employed.

proximate organic analysis, that is, of the separation of an organic mixture into its immediate components.

For the separation of the numerous volatile substances contained in coal-tar, advantage is taken of the difference in their boiling-points.

A large quantity of the tar is distilled in an iron retort, when water passes over, holding salts of ammonia in solution, and accompanied by a brown oily offensive liquid which collects upon the surface of the water. This is a mixture of the hydrocarbons, which are lighter than water, viz., benzene, toluene, xylene, and isocumene, all having a specific gravity of about 0.85. 100 parts of the tar yield, at most, 10 parts of this *light oil*.

As the distillation proceeds and the temperature rises, a yellow oil distils over, which is heavier than water, and sinks in the receiver. This oil, commonly called *dead oil*, is much more abundant than the light oil, amounting to one-fourth of the weight of the tar, and contains those constituents of the tar which have a high specific gravity and boiling-point, particularly naphthalene, aniline, quinoline, and carbolic acid. The proportion of naphthalene in this oil increases with the progress of the distillation, as would be expected from its high boiling-point, so that the last portions of the oil which distil over become nearly solid on cooling. When this is the case, the distillation is generally stopped, and a black viscous residue is found in the retort, which constitutes *pitch*, and is employed for the preparation of Brunswick black and of asphalt for paving.

The light oil which first passed over is rectified by a second distillation, and is then sent into commerce under the name of *coal-naphtha*, a quantity of the heavy oil being left in the retort, the lighter oils having lower boiling-points.

This coal-naphtha may be further purified by shaking it with sulphuric acid, which removes several of the impurities, whilst the pure naphtha collects on the surface when the mixture is allowed to stand. When this is again distilled it yields the *rectified coal-naphtha*.

The distillation of cannel coal, and of various minerals nearly allied to coal, at low temperatures, is now extensively carried on for the manufacture of paraffin and paraffin oil (see *Paraffin*).

Coal-tar dyes.—The first dye ever manufactured from aniline on a large scale was that known as *mauve*,* or *aniline purple*, which is obtained by dissolving aniline in diluted sulphuric acid, and adding solution of bichromate of potash, when the liquid gradually becomes dark-coloured, and deposits a black precipitate which is filtered off, washed, boiled with coal-naphtha to extract a brown substance, and afterwards treated with hot alcohol, which dissolves the mauve. The chemical change by which the aniline has been converted into this colouring-matter cannot at present be clearly traced, but the basis of the colour has been found to be a substance which has the composition $C_{27}H_{24}N_4$, and has been termed *mauvéine*. It forms black shining crystals, resembling specular iron ore, which dissolve in alcohol, forming a violet solution, and in acids, with production of the purple colour. Mauvéine combines with the acids to form salts; its alcoholic solution even absorbs carbonic acid gas. The *hydrochloride of mauvéine*, $C_{27}H_{24}N_4 \cdot 2HCl$, forms prismatic needles with a green metallic lustre.

Very brilliant red dyes are obtained from commercial aniline by the action of carbon tetrachloride, stannic chloride, ferric chloride, cupric chloride, mercuric nitrate, corrosive sublimate, and arsenic acid. It will be noticed that all these agents are capable of undergoing reduction to a lower state of oxidation or chlorination, indicating that the chemical change concerned in the transformation of aniline into aniline-red is one in which the aniline is acted on by oxygen or chlorine. The easiest method of illustrating the production of aniline red on the small scale consists in heating a few drops of aniline in a test-tube with a fragment of corrosive sublimate (mercuric chloride), which soon fuses and acts upon the aniline to form an intensely red mass composed of aniline red, calomel, and various secondary products. By heating this mixture with alcohol, the red dye is dissolved, and a skein of silk or wool dipped into the liquid becomes dyed of a fine red, which is not removed by washing.

On the large scale, *magenta* (as aniline red is commonly termed) is generally prepared by heating aniline to about 320° F. (160° C.) with arsenic acid, when a dark semi-solid mass is obtained, which becomes hard and brittle on cooling, and exhibits a green metallic reflection. This mass contains, in addition to aniline

* French for marshmallow, in allusion to the colour of the flower.

red, several secondary products of the action, and arsenious acid. On boiling it with water, a splendid red solution is obtained, and a dark resinous or pitchy mass is left. If common salt be added to the red solution as long as it is dissolved, the bulk of the colouring-matter is precipitated as a resinous mass, which may be purified from certain adhering matters by drying and boiling with coal-naphtha. The red colouring-matter is the arsenate of a *colourless* organic base, which has been called *rosaniline* (p. 722). If the red solution of arsenate of rosaniline be decomposed with calcium hydroxide suspended in water, a pinkish precipitate is obtained, which consists of rosaniline mixed with calcium arsenate, and the solution entirely loses its red colour (*cf.* p. 722).

By treating the precipitate with a small quantity of acetic acid, the rosanilice is converted into *rosaniline acetate* ($C_{20}H_{19}N_3.C_2H_4O_2$), forming a red solution, which may be filtered off from the undissolved calcium arsenate. On evaporating the solution to a small bulk, and allowing it to stand, the acetate is obtained in crystals which exhibit the peculiar green metallic lustre of the wing of the rose-beetle, characteristic of the salts of rosaniline. This salt is the commonest commercial form of magenta; its colouring power is extraordinary, a very minute particle imparting a red tint to a large volume of water. Silk and wool easily extract the whole of the colouring-matter from the aqueous solution, becoming dyed a fast and brilliant crimson; cotton and linen, however, have not so strong an attraction for it, so that if a pattern be worked in silk upon a piece of cambric, which is then immersed in a solution of magenta and afterwards washed in hot water, the colour will be washed out of the cambric; but the red silk pattern will be left.

Water dissolves but little rosaniline; alcohol dissolves it abundantly, forming a deep red solution. Rosaniline forms two classes of salts with acids, those with 1 molecule of acid (*monacid* salts) being crimson, and those with three molecules (*triacid* salts) having a brown colour. Thus, if colourless rosaniline be dissolved in a little dilute hydrochloric acid, a red solution is obtained, which contains the monacid rosaniline hydrochloride, $C_{20}H_{19}N_3.HCl$; but if an excess of hydrochloric acid be added, the red colour disappears, and a brown solution is obtained, from which the triacid hydrochloride, $C_{20}H_{19}N_3.3HCl$, may be crystallised in brown red needles.

For experimental illustration of the properties of rosaniline, the liquid obtained by boiling a solution of the acetate with a slight excess of lime diffused in water, and filtering while hot, is very well adapted. The solution has a yellow colour, and may be preserved in a stoppered bottle without alteration. If air be breathed into it through a tube, the liquid becomes red from production of rosaniline carbonate. Characters painted on paper with a brush dipped in the solution are invisible at first, but gradually acquire a beautiful rose colour.

The other properties of rosaniline will be found described at p. 722.

Aniline-yellow, or *chrysaniline* (from χρύσεος, *golden*), is found among the secondary products obtained in the preparation of aniline red. It forms a bright yellow powder, resembling chrome-yellow, and having the composition $C_{20}H_{17}N_3$. It is nearly insoluble in water, but dissolves in alcohol. Chrysaniline has basic properties, and dissolves in acids, forming salts. On dissolving it in diluted hydrochloric acid, and mixing the solution with the concentrated acid, a scarlet crystalline precipitate of *chrysaniline hydrochloride* ($C_{20}H_{17}N_3.2HCl$) is obtained, which is insoluble in strong hydrochloric acid, but very soluble in water. A characteristic feature of chrysaniline is the sparing solubility of its nitrate. Even from a dilute solution of the hydrochloride, nitric acid precipitates chrysaniline nitrate ($C_{20}H_{17}N_3.HNO_3$) in ruby-red needles.

Aniline-blue is produced as described on p. 723.

The hydrochloride is an ordinary commercial form of aniline-blue; it has a brown colour, refuses to dissolve in water, but yields a fine blue solution in alcohol.

DYEING AND CALICO-PRINTING.

599. The object of the dyer being to fix certain colouring-matters permanently in the fabric, his processes would be expected to vary with the nature of the latter and of the colour to be applied to it. In order that uniformity of colour and its perfect penetration into the fibre may be obtained, it is evident that the colouring-matter must always be employed in a state of solution; and it must be rendered

fast, or not removable by washing, by assuming an insoluble condition in the fibre.

The simplest form of dyeing is that in which the fibre itself forms an insoluble compound with the colouring-matter. Thus, if a skein of silk be immersed in a solution of indigo in sulphuric acid, it removes the whole of the colouring-matter from the liquid, and may then be washed with water without losing colour; but if the same experiment be tried with cotton, the indigo will not be withdrawn from the solution, and when the cotton has been well squeezed and rinsed with water, it will become white again. It may be stated generally, that the animal fabrics (silk and wool) will absorb and retain colouring-matters with much greater facility than vegetable fabrics (cotton and linen). In the absence of so powerful an attraction between the fibre and the colouring-matter, it is usual to impregnate the fabric with a *mordant* or substance having an attraction for the colour, and capable of forming an insoluble combination with it, so as to retain it permanently attached to the fabric. Thus, if a piece of cotton be boiled in a solution of acetate of alumina, the alumina will be precipitated in the fibre; and if the cotton be then soaked in solution of cochineal or of logwood, the red colouring-matter will form an insoluble compound (or *lake*) with the alumina, and the cotton will be dyed of a fast red colour.

Another method of fixing the colour in the fabric consists in impregnating the latter with two or more liquids in succession, by the admixture of which the colour may be produced in an insoluble state. If a piece of any stuff be soaked in solution of ferric chloride, and afterwards in potassium ferrocyanide, the Prussian blue which is precipitated in the fibre will impart a fast blue tint.

An indispensable preliminary step to the dyeing of any fabric is the removal of all natural grease or colouring-matter, which is effected by processes varying with the nature of the fibre, and is preceded, in the cases of cotton and woollen materials which are to receive a pattern, by certain operations of shaving and singeing for removing the short hairs from the surface.

From linen and cotton, the extraneous matters (such as grease and resin) are generally removed by weak solutions of carbonate of potassium or of sodium, and the fabrics are afterwards bleached by treatment with chloride of lime (p. 183).

But since the fibres of silk and wool are much more easily injured by alkalies and by chlorine, greater care is requisite in cleansing them. Silk is boiled with a solution of white soap to remove the *gum*, as it is technically termed; but the natural grease, *suint* or *yolk*, is extracted from wool by soaking at a moderate temperature in a weak bath either of soap or of ammoniacal (putrefied) urine. Both silk and wool are bleached by sulphurous acid (p. 220).

Among the *red dyes* the most important are *madder*, *alizarine*, *Brazil wood*, *cochineal*, *lac*, and the *aniline reds*.

In dyeing red with madder or Brazil wood, the linen, cotton, or wool is first mordanted by boiling in a solution containing alum and bitartrate of potash, when it combines with a part of the alumina, and on plunging the stuff into a hot infusion of madder, the colouring-matter forms an insoluble combination with that earth.

To dye Turkey-red, the stuff is also mordanted with alum, but has previously to undergo several processes of treatment with oil and with galls, the necessity of which is satisfactorily established in practice, though it is not easy to explain their action. The colour is finally brightened by boiling the stuff with chloride of tin.

Woollen cloth is dyed scarlet with lac or cochineal, having been first mordanted by boiling in a mixture of perchloride of tin and bitartrate of potash.

The aniline colours (see p. 794) are employed for dyeing silk and wool, either without any mordant or with the help of albumin.

Blues are generally dyed with *indigo* (p. 761), or with *Prussian blue*; in the latter case the stuff is steeped successively in solutions of a salt of peroxide of iron and of potassium ferrocyanide. *Aniline blue* is also much employed for silk and woollen fabrics.

The principal *yellow dyes* are *weld*, *quercitron*, *fustic*, *annatto*, *chrysaniline*, and *lead chromate*. For the first four colouring-matters aluminous mordants are generally applied. Lead chromate is produced in the fibre of the stuff, which is soaked for that purpose, first in a solution of acetate or nitrate of lead, and then

in potassium chromate. Carbazotic or *picric acid* (p. 711) is also sometimes employed as a yellow dye.

In dyeing *blacks* and *browns*, the stuffs are steeped first in a bath containing some form of tannin (p. 610), such as infusion of *galls*, *sumach*, or *catechu*, and afterwards in a solution of salt of *iron*, different shades being produced by the addition of indigo, of copper sulphate, &c.

The art of *calico printing* differs from that of dyeing in that the colour is required to be applied only to certain parts of the fabric so as to produce a pattern or design either of one or of several colours.

A common method of printing a coloured pattern on a white ground consists in impressing the pattern by passing the stuff under a roller, to which an appropriate mordant thickened with British gum (p. 736) is applied. The stuff is then *dunged—i.e.*, drawn through a mixture of cow-dung and water, which appears to act by removing the excess of the mordant, and afterwards immersed in the hot dye-bath, when the colour becomes permanently fixed to the mordanted device, but may be removed from the rest of the stuff by washing.

If the pattern be printed with a solution of acetate of iron, and the stuff immersed in a madder-bath, a lilac or black pattern will be obtained according to the strength of the mordant employed. By using acetate of alumina as a mordant, the madder-bath would give a red pattern.

A process which is the reverse of this is sometimes employed, the pattern being impressed with a *resist*, that is, a substance which will prevent the stuff from taking the colour in those parts which have been impregnated with it. For example, if a pattern be printed with thickened tartaric or citric acid, and the stuff be then passed through an aluminous mordant, the pattern will refuse to take up the alumina, and subsequently the colour from the dye-bath. Or a pattern may be printed with nitrate of copper, and the stuff passed through a bath of reduced indigo (p. 762), when the nitrate of copper will oxidise the indigo, and, by converting it into the blue insoluble form, will prevent it from sinking into the fibre of those parts to which the nitrate has been applied, whilst elsewhere the fibre, having become impregnated with the white indigo, acquires a fast blue tint when exposed to the air.

Sometimes the stuff is uniformly dyed, and the colour discharged in order to form the pattern. A white pattern is produced upon a red (madder) or blue (indigo) ground by printing with a thickened acid discharge, and passing the stuff through a weak bath of chloride of lime, which removes the colour from those parts only which were impregnated with the acid (p. 183). By adding lead nitrate to the acid discharge, and finally passing the stuff through a solution of potassium chromate, a yellow pattern (lead chromate) may be obtained upon the madder-red ground. By applying nitric acid as a discharge, a yellow pattern may be obtained upon an indigo ground (p. 91).

Very brilliant designs are produced by mordanting the stuff in a solution of stannate of potassium or sodium (p. 453), and immersing it in dilute sulphuric acid, which precipitates the stannic acid in the fibre.

When the thickened colouring-matters are printed on in patterns and *steamed* an insoluble compound is formed between the colour and the stannic acid.

It is evident that, by combining the principles of which an outline has just been given, the most varied parti-coloured patterns may be printed.

TANNING.

600. When infusion of nut-galls is added to a solution of gelatine, the latter combines with the tannic acid, and a bulky precipitate is obtained. If a piece of skin, which has approximately the same ultimate composition as gelatine, be placed in the infusion of nut-galls, it will absorb the whole of the tannic acid and become converted into leather, which is much tougher than the raw skin, less permeable by water, and not liable to putrefaction.

The first operation in the conversion of hides into leather, after they have been cleansed, consists in soaking them for three or four weeks in pits containing lime and water, which saponifies the fat and loosens the hair. The same object is sometimes attained by allowing the hides to enter into putrefaction, when the ammonia produced has the same effect as the lime. The loosened hair is then scraped off, and the hides are soaked in water, which removes adhering lime. A further effect of the lime is to open the pores of the skin, so as to fit it to receive

the tanning liquid; if lime have not been used, a dilute acid should be employed to effect the same purpose.

The tanning material generally employed for hides is the infusion of oak bark, which contains *querci-tannic acid*, very similar in properties to tannic acid. The hides are soaked in an infusion of oak bark for about six weeks, being passed in succession through several pits, in which the strength of the infusion is gradually increased. They are then packed in another pit with alternate layers of coarsely ground oak bark; the pit is filled with water and left at rest for three months, when the hides are transferred to another pit and treated in the same way; but, of course, the position of the hides will now be reversed—that which was uppermost, and in contact with the weakest part of the tanning liquor, will now be at the bottom. After the lapse of another three months the hide is generally found to be tanned throughout, a section appearing of a uniform brown colour. It has now increased in weight from 30 to 40 per cent. The chemical part of the process being thus completed, the leather is subjected to certain mechanical operations to give it the desired texture. For tanning the thinner kinds of leather, such as morocco, a substance called *sumach* is used, which consists of the ground shoots of the *Rhus coriaria*, and contains a large proportion of tannic acid.

Morocco leather is made from goat and sheep skins, which are denuded of hair by liming in the usual way, but the adhering lime is afterwards removed by means of a bath of sour bran or flour. In order to tan the skin so prepared, it is sewn up in the form of a bag, which is filled with infusion of sumach, and allowed to soak in a vat of the infusion for some hours. A repetition of the process, with a stronger infusion, is necessary; but the whole operation is completed in twenty-four hours. The skins are now washed and dyed, except in the case of red morocco, which is dyed before tanning, by steeping it first in alum or chloride of tin, as a mordant, and afterwards in infusion of cochineal. Black morocco is dyed with acetate of iron, which acts upon the tannic acid. The aniline dyes are now much employed for dyeing morocco.

The *kid* of which gloves are made is not actually tanned, but submitted to an elaborate operation called *tawing*, the chief chemical features of which are the removal of the excess of lime,* and opening the pores of the skin by means of a sour mixture of bran and water, in which lactic acid is the agent; and the subsequent impregnation of the porous skin with aluminium chloride, by steeping it in a hot bath containing alum and common salt. The skins are afterwards softened by kneading in a mixture containing alum, flour, and the yoke of eggs. The putrefaction of the skin is as effectually prevented by the aluminium chloride as by tanning.

Wash-leather and *buckskin* are not tanned, but *shamoyed*, which consist in sprinkling the prepared skins with oil, folding them up, and *stocking* them under heavy wooden hammers for two or three hours. When the grease has been well forced in, they are exposed in a warm atmosphere, to promote the drying of the oil by absorption of oxygen (p. 798). These processes having been repeated the requisite number of times, the excess of oil is removed by a weak alkaline bath, and the skins are dried and rolled. The buff colour of wash-leather is imparted by a weak infusion of sumach.

Parchment is made by stretching lamb or goat skin upon a frame, removing the hair by lime, and scraping, as usual, and afterwards rubbing with pumice-stone, until the proper thickness is acquired.

OILS AND FATS.

601. A very remarkable feature in the history of the fats is the close resemblance in chemical composition and properties which exists between them, whether derived from the vegetable or the animal kingdom. They all contain two or more neutral substances which furnish glycerine when saponified, together with some of the acids of the acetic series or of series closely allied to it.

One of the most useful vegetable fatty matters is *palm oil*, which is extracted by boiling water from the crushed fruit of the *Elais guineensis*, an African palm. It is a semi-solid fat, which becomes more solid when kept, since it then undergoes a species of fermentation, excited apparently by an albuminous substance contained in it, in consequence of which the palmitin ($C_{51}H_{98}O_6$) is converted into

* Polysulphides of sodium or calcium are sometimes employed for removing the hair.

glycerine and palmitic acid. The bleaching of palm oil is effected by the action of a mixture of sulphuric or hydrochloric acid and potassium dichromate, which oxidises the yellow colouring-matter.

Cocoa-nut oil is also semi-solid, and is remarkable for the number of acids of the acetic series which it yields when saponified—viz., caproic, caprylic, rutic, lauric, myristic, and palmitic.

These fats are chiefly used in the manufacture of soap and candles.

Salad oil, or *sweet oil* (*olive oil*), is obtained by crushing olives, and an inferior kind which is used for soap is obtained by boiling the crushed fruit with water. When exposed to a temperature of about 32° F. a considerable portion of the oil solidifies; this solid portion is generally called *margarin* ($C_{54}H_{104}O_8$); it is much less soluble in alcohol than stearin is, though more so than palmitin. When saponified, margarin yields glycerine and *margaric acid* ($C_{17}H_{34}O_2$). This acid appears to be really composed of stearic and palmitic acids, into which it may be separated by repeated crystallisation from alcohol, when the palmitic acid is left in solution. The fusing-point of margaric acid is 140° F., that of stearic being 159°, and that of palmitic, 144°, but a mixture of 10 parts of palmitic with 1 part of stearic acid fuses at 140°.

That portion of the olive oil which remains liquid below 32° F. consists of *olein* ($C_{57}H_{104}O_6$), and forms nearly three-fourths of its weight.

It is well known that salad oil becomes rancid and exhales a disagreeable odour after being kept for some time. This appears to be due to a fermentation similar to that noticed in the case of palm oil, originally started by the action of atmospheric oxygen upon albuminous matters present in the oil; the neutral fatty matters are thus partly decomposed, as in saponification; their corresponding acids being liberated, and giving rise (in the case of the higher members of the acetic series, such as caproic and valerianic) to the disagreeable odour of rancid oil. By boiling the altered oil with water, and afterwards washing it with a weak solution of soda, it may be rendered sweet again.

Almond oil, extracted by a process similar to that employed for olive oil, is also very similar in composition; but *colza oil* (*rape oil*), obtained from the seeds of the *Brassica oleifera*, contains only half its weight of olein, and hence solidifies more readily than the others.

Colza oil is largely used for burning in lamps, and undergoes a process of purification from the mucilaginous substances which are extracted with it from the seed, and leave a bulky carbonaceous residue when subjected to destructive distillation in the wick of the lamp. To remove these, the oil is agitated with about 2 per cent. of oil of vitriol, which carbonises the mucilaginous substances, but leaves the oil untouched. When the carbonaceous flocks have subsided, the oil is drawn off, washed to remove the acid, and filtered through charcoal.

Linseed oil, obtained from the seeds of the flax plant, is much richer in olein than any of the foregoing, exhibiting no solidification till cooled to 15° or 20° F. below the freezing-point. It exhibits, however, in a far higher degree, a tendency to become solid when exposed to the air, which has acquired for it the name of a *drying oil*, and renders it of the greatest use to painters. This solidification is attended with absorption of oxygen, which occurs so rapidly in the case of linseed oil that spontaneous combustion has been known to take place in masses of rag or tow which have been smeared with it.*

The tendency of linseed oil to solidify by exposure is much increased by heating it with about $\frac{1}{70}$th of litharge, or $\frac{1}{10}$th of black oxide of manganese; these oxides are technically known as *dryers*, and oil so treated is called *boiled linseed oil*. The action of these metallic oxides is not well understood.

The strong drying tendency of linseed oil is supposed to be due to a peculiarity in the olein, which is said not to be ordinary olein, but to furnish a different acid, *linoleic acid*, when saponified. When linseed oil is exposed for some time to a high temperature, it becomes viscous and treacly, and is used in this state for the preparation of printing ink. If the viscous oil be boiled with dilute nitric acid, it is converted into *artificial caoutchouc*, which is used in the manufacture of surgical instruments. This property appears to be connected with the drying qualities of the oil.

Castor oil, obtained from the seeds of *Ricinus communis*, also yields a peculiar

* During the oxidation, a volatile compound is formed which resembles acrolein in smell, and colours unsized paper brown. It has been suggested that the brown colour and musty smell of old books may be due to the oxidation of the oil in the printing-ink.

acid when saponified, termed *ricinoleic* ($H{\cdot}C_{18}H_{33}O_3$), containing one more atom of oxygen than oleic acid, which it much resembles. The destructive distillation of castor oil yields *œnanthic acid* ($H{\cdot}C_7H_{13}O_2$) and *œnanthol*, or *œnanthic aldehyde* ($C_7H_{14}O$), and by distilling it with caustic potash, caprylic alcohol ($C_8H_{18}O$) is obtained. As in the case of olive oil, the *cold-drawn* castor oil, which is expressed from the seeds without the aid of heat, is much less liable to become rancid. Castor oil is much more soluble in alcohol than is any other of the fixed oils.

The various *fish oils*, such as seal and whale oil, also consist chiefly of olein, and appear to owe their disagreeable odour to the presence of certain volatile acids, such as valerianic.

Cod-liver oil appears to contain, in addition to olein and stearin, a small quantity of *acetin* ($C_9H_{14}O_6$), which yields acetic acid and glycerine when saponified. Some of the constituents of bile have also been traced in it, as well as minute quantities of iodine and bromine.

Butter contains about half its weight of solid fat, which consists in great part of palmitin and stearin, but contains also *butin*, which yields glycerine and *butic acid* ($H{\cdot}C_{20}H_{39}O_2$) when saponified. The liquid portion consists chiefly of olein. Butter also contains small quantities of butyrin, caproin, and caprin, which yield, when saponified, glycerine and butyric ($H{\cdot}C_4H_7O_2$), caproic ($H{\cdot}C_6H_{11}O_2$), and capric ($H{\cdot}C_{10}H_{19}O_2$) acids, distinguished for their disagreeable odour. Fresh butter has very little odour, being free from these volatile acids, but if kept for some time, especially if the casein of the milk has been imperfectly separated in its preparation, spontaneous resolution of these fats into glycerine and the volatile disagreeable acids occurs. By salting the butter this change is in great measure prevented. *Margarine*, the butter substitute, is made from the less solid portion of mutton suet.

The fat of the sheep and ox (*suet*, or, when melted, *tallow*) consists chiefly of stearin, whilst in that of the pig (*lard*) olein predominates to about the same extent as in butter. Palmitin is also present in these fats. *Benzoated lard* contains some gum benzoin, which prevents it from becoming rancid.

Human fat contains chiefly olein and margarin (or, if we do not admit the independent existence of the latter, palmitin and stearin).

Sperm oil, which is expressed from the spermaceti found in the brain of the sperm whale, owes its peculiar odour to the presence of a fat which has been called *phocenin*, but which appears to be *valerin*, as it yields glycerine and valerianic acid ($H{\cdot}C_5H_9O_2$) when saponified.

The beautiful solid crystalline fat, known as *spermaceti* or *cetin*, differs widely from the ordinary fatty matters, for when saponified (which is not easily effected), it yields no glycerine, but in its stead cetyl alcohol (p. 570).

The soap prepared from spermaceti, when decomposed by an acid, yields palmitic acid ($H{\cdot}C_{16}H_{31}O_2$).

Ambergris, used in perfumery, is a fatty substance found in the intestines of the spermaceti whale. Boiling alcohol extracts from it about 80 per cent. of *ambrein*.

Chinese wax, the produce of an insect of the Cochineal tribe, is analogous in its chemical constitution to spermaceti. When saponified by fusion with caustic potash, it yields *cerotin*, or *ceryl alcohol* ($C_{27}H_{55}{\cdot}OH$), and *cerotic acid* ($H{\cdot}C_{27}H_{53}O_2$). Cerotic acid is also contained in ordinary bees'-wax, from which it may be extracted by boiling alcohol, and crystallised as the solution cools. It forms about two-thirds of the weight of the wax. Cerotic acid is found among the products of oxidation of paraffin by chromic acid.

Bees'-wax also contains about one-third of its weight of *myricin* ($C_{46}H_{92}O_2$), a substance analogous to spermaceti, which yields, when saponified, palmitic acid and *melissin*, or *myricyl alcohol* ($C_{30}H_{61}{\cdot}OH$). The colour, odour, and tenacity of bees'-wax appear to be due to the presence of a greasy substance called *cerolein*, which forms about $\frac{1}{10}$ of the wax, and has not been fully examined. The *tree wax* of Japan is said to be pure palmitin.

Wax is bleached for the manufacture of candles, by exposing it in thin strips or ribands to the oxidising action of the atmosphere, or by boiling it with nitrate of soda and sulphuric acid. Chlorine also bleaches it, but displaces a portion of the hydrogen in the wax, taking its place and causing the evolution of hydrochloric acid vapours when the wax is burnt.

The following table includes the principal fatty bodies and their corresponding acids, with their fusing-points:—

Neutral Fats.	Formula.	Chief Source.	Fusing-point, Fahr.	Fatty Acids.	Formula.	Fusing-point, Fahr.
Stearin	$C_{57}H_{110}O_6$	Tallow	125° to 157°	Stearic	$C_{18}H_{36}O_2$	159°
Palmitin	$C_{51}H_{98}O_6$	Palm oil	114° to 145°	Palmitic	$C_{16}H_{32}O_2$	144°
Margarin	$C_{54}H_{104}O_6$	Olive oil	116°	Margaric	$C_{17}H_{34}O_2$	140°
Olein	$C_{57}H_{104}O_6$	,,	Below 32°	Oleic	$C_{18}H_{34}O_2$	40°
Cetin	$C_{32}H_{64}O_2$	Spermaceti	120°	Palmitic	$C_{16}H_{32}O_2$	144°
Myricin	$C_{46}H_{92}O_2$	Bees'-wax	162°	,,	,,	,,

CHEMISTRY OF SOAP.

602. The manufacture of soap affords an excellent instance of a process which was in use for centuries before anything was known of the principles upon which it is based, for it was not till the researches of Chevreul were published in 1813 that any definite ideas were entertained with respect to the composition of the various fats and oils from which soaps are made.

The investigations of Chevreul are conspicuous among the labours which have contributed in so striking a manner to the rapid advancement of chemistry during the nineteenth century; undertaken when the chemistry of organic substances had scarcely advanced beyond the dignity of an art, when the principles of classification were almost entirely empirical, and hardly any research had been published which would serve as a model, these investigations reflect the remarkable sagacity and accuracy of their author.

The sense of our obligation to this eminent chemist is further increased, when we remember that the ultimate analysis of organic substances was then effected by a very difficult and laborious process, whilst the doctrine of combining proportions was so imperfectly understood, that it could afford but little assistance in confirming or interpreting the result of analysis.

All soaps are formed by the action of the alkalies upon the oil and fats.

In the manufacture of soap, potash and soda are the only alkalies employed, the former for soft, the latter for hard soaps.

The fatty matters used by the soap-maker are chiefly tallow, palm oil, cocoa-nut oil, and kitchen stuff, for hard soaps, and seal oil and whale oil for soft soaps.

In the manufacture of hard soap, the alkali is prepared by decomposing or *caustifying* sodium carbonate (soda-ash) with slaked lime, $Na_2CO_3 + Ca(OH)_2 = CaCO_3 + 2NaOH$, the clear solution of sodium hydroxide, or *soda-ley*, being drawn off from the insoluble calcium carbonate.

The tallow is at first boiled with a weak soda-ley,* because the soap which is formed is insoluble in a strong alkaline solution, and would enclose and protect a quantity of undecomposed tallow; in proportion as the saponification proceeds, stronger leys are added, until the whole of the grease has disappeared. In order to separate the soap which is dissolved, advantage is taken of the insolubility of soap in solution of salt; a quantity of common salt being thrown into the boiler. the soap rises to the surface, when the *spent ley* is drawn off from below, and the soap transferred to iron moulds that it may harden sufficiently to be cut up into bars.

In order to understand the chemistry of this process, it is necessary to know that tallow contains two fatty substances, one of which, *stearin*† ($C_{57}H_{110}O_6$), is solid, and the other, *olein* ($C_{57}H_{104}O_6$), liquid, the quantity of stearin being about thrice that of olein.

When these fats are acted upon by soda, they undergo decomposition, furnishing stearic and oleic acids, which combine with the soda to form soap, whilst a peculiar sweet substance, termed *glycerine*, passes into solution; the nature of the decomposition in each case will be understood from the following equations—

* Soap is now sometimes made by the action of the sodium carbonate upon the fat, thus saving the expense of caustifying (Morfit's process).

† Στέαρ, *tallow*.

$$\underset{\text{Stearin.}}{C_3H_5\cdot(C_{18}H_{35}O)_3\cdot O_3} + 3NaOH = \underset{\text{Sodium stearate.}}{3Na(C_{18}H_{35}O)O} + \underset{\text{Glycerine.}}{C_3H_8O_3}$$

$$\underset{\text{Olein.}}{C_3H_5\cdot(C_{18}H_{33}O)_3\cdot O_3} + 3NaOH = \underset{\text{Sodium oleate.}}{3Na(C_{18}H_{33}O)O} + \underset{\text{Glycerine;}}{C_3H_8O_3}$$

so that the soap obtained by boiling tallow with soda is a mixture of the sodium stearate with about a third of its weight of sodium oleate and 20 to 30 per cent. of water.

Palm oil is composed chiefly of *palmitin* ($C_{51}H_{98}O_6$), a solid fat which is resolved, by boiling with soda, into sodium palmitate (palm oil soap) and glycerine; $\underset{\text{Palmitin.}}{C_3H_5\cdot(C_{16}H_{31}O)_3\cdot O_3} + 3NaOH = \underset{\text{Sodium palmitate.}}{3Na(C_{16}H_{31}O)O} + \underset{\text{Glycerine.}}{C_3H_8O_3}$

In the fish oils the predominant constituent is olein, so that when boiled with potassium hydroxide, they yield potassium oleate ($KC_{18}H_{33}O_2$), which composes the chief part of *soft soap*.

Castile soap is made from olive oil, which contains olein and a solid fat known as *margarin*. The latter appears to be really composed of palmitin and stearin, so that the Castile soap is a mixture of oleate, palmitate, and stearate of sodium.

The peculiar appearance of *mottled soap* is caused by the irregular distribution of a compound of the fatty acid with oxide of iron, which arranges itself in veins throughout the mass. If the soap contained too much water, so as to render it very fluid when transferred to the moulds, this iron compound would settle down to the bottom, leaving the soap clear, so that the mottled appearance is often regarded as an indication that the soap does not contain an undue proportion of water; it is imitated, however, by stirring into the pasty soap some ferrous sulphate and a little impure ley containing sodium sulphide, so as to produce the dark sulphide of iron by double decomposition.*

In the manufacture of *yellow soap*, in addition to tallow and palm oil, a considerable proportion of common rosin (see p. 560) is added to the soap shortly before it is finished. *Soft soap* is not separated from the water by salt like hard soap, but is evaporated to the required consistency. Transparent soaps are obtained by drying hard soap, dissolving it in hot spirit of wine, and pouring the strong solution into moulds after the greater part of the spirit has been distilled off. *Silicated soap* is a mixture of soap with silicate of soda. *Glycerine soap* is prepared by heating the fat with alkali and a little water at about 400° F. for two or three hours, and running the mass at once into moulds. It is, of course, a mixture of soap and glycerine.

The proportion of water in soap is very variable, some specimens containing between 70 and 80 per cent. The smallest proportion is about 30 per cent.

The theory of saponification, stated above, has received the strongest confirmation within the last few years, by the synthetic production of the fats from glycerine and the fatty acids formed in their saponification.

CANDLES.

603. Since tallow fuses at about 100° F., and stearic acid not below 159°, it is evident that, independently of other considerations, the latter would be better adapted for the manufacture of candles, for such candles would never soften at the ordinary atmospheric temperature in any climate, and would have much less tendency to *gutter* in consequence of the excessive fusion of the fuel around the base of the wick. The gases furnished by the destructive distillation of stearic acid in the wick of the candle burn with a brighter flame than those produced from tallow. Accordingly, the manufacture of stearin (or more correctly, stearic acid) candles† has now become a very important and instructive branch of industry.

The original method of separating the stearic acid from tallow on the large scale consisted in mixing melted tallow with lime and water, and heating the mixture for some time at 212° F. by passing steam through it.

The tallow was thus converted into the insoluble stearate and oleate of calcium, which was drained from the solution containing the glycerine, and decomposed by

* A soap which contains more than 30 per cent. of water is said not to admit of mottling.

† *Composite candles* are made of a mixture of stearic and palmitic acid.

sulphuric acid. The mixture of stearic and oleic acids thus obtained was cast into thin slabs, which were packed between pieces of coco-nut matting, and well squeezed in a hydraulic press, which forced out the oleic acid, leaving the stearic and palmitic acids in a fit state for the manufacture of candles.

The separation of the solid fatty acids from tallow and other fats may also be effected by the action of sulphuric acid, a process extensively applied in this country to palm and coco-nut oils. These fats are mixed in copper boilers with about one-sixth of their weight of concentrated sulphuric acid, and heated by steam at about 350° F. for some hours, when part of the glycerine is converted into sulphoglyceric acid ($C_3H_8O_3 \cdot SO_3$), and the remainder is decomposed by the sulphuric acid, carbonic and sulphurous acid gases being disengaged, whilst a dark-coloured mixture of palmitic, stearic and oleic acid is left. A part of the oleic acid becomes converted in this process into *elaidic acid*, which has the same composition, but differs from oleic acid in fusing at about 113° F., so that the amount of solid acid obtained by this process is much increased. This mixture is well washed from the adhering sulphuric and sulphoglyceric acids, and transferred to a copper still into which a current of steam is passed, which has been raised to about 600° F. by passing through hot iron pipes. These fatty acids could not be distilled alone without decomposition, but under the influence of a current of steam they pass over readily enough, leaving a black pitchy residue in the retort, which is employed in making black sealing-wax, and for other useful purposes.

The distilled fatty acids are broken up and pressed between coco-nut matting to remove the oleic acid.

One great advantage of this process, which is commonly, though incorrectly, styled the *saponification by sulphuric acid*, is its allowing the conversion of the worst kinds of refuse fat into a form fit for the manufacture of candles; thus, the fat extracted from bones in the manufacture of glue, and that removed from wool in the scoring process, may be turned to profitable account.

It will be remarked that in this process the palmitic, stearic, and oleic acids are formed from the palmitin, stearin, and olein existing in the fats, by the assimilation of the elements of water and the subsequent separation of glycerine, just as in the ordinary process of saponification by means of alkalies.

Strictly speaking, the action appears to consist of two stages; for when concentrated sulphuric acid is allowed to act upon the natural fats in the cold, it combines with each of their ingredients, forming the acids known as sulphostearic, sulphopalmitic, sulpholeic, and sulphoglyceric, which are soluble in water, though not (with the exception of the last) in water containing sulphuric acid.

The second stage consists in the decomposition of the sulpho-fatty acids by the high temperature in contact with steam, the sulphoglyceric acid having been in great measure decomposed into secondary products before the distillation is commenced.

Within the last few years, the extraction of the solid acids from the natural fats has been effected by a process known as *saponification by steam*, which allows the glycerine also to be obtained in a pure state. It is only necessary to subject the fat, in a distillatory apparatus, to the action of steam, at a temperature of about 600° F., to cause both the fatty acids and the glycerine to distil over; the former may be separated as usual into solid and liquid portions by pressure, whilst the glycerine, which is obtained in aqueous solution below the layer of fatty acids, is concentrated by evaporation, and sent into commerce as a very sweet colourless viscid liquid. The saponification of palmitin, for instance, by steam, would be represented by the equation—

$$\underset{\text{Palmitin.}}{C_3H_5 \cdot (C_{16}H_{31}O_2)_3} + 3H_2O = \underset{\text{Palmitic acid.}}{3(H \cdot C_{16}H_{31}O_2)} + \underset{\text{Glycerine.}}{C_3H_5(HO)_3}$$

STARCH.

604. Starch is manufactured chiefly from potatoes, wheat, and rice, the solid portion of which consists chiefly of starch, as appears in the following result of analysis:—

	Potatoes.	Wheat.	Rice.
Starch	20.2	60.8	83.0
Water	75.9	12.1	5.0
Gluten		10.5	6.0
Albumin	2.3	2.0	
Dextrin and sugar		10.5	1.0
Woody fibre	0.4	1.5	4.8
Oily matter	0.2	1.1	0.1
Mineral matter	1.0	1.5	0.1
	100.0	100.0	100.0

In order to extract the starch, the potatoes are rasped to a pulp, which is washed upon a sieve under a stream of water, as long as the latter is rendered milky by the starch suspended in it, the woody fibre being left behind upon the sieve. The milky liquid is allowed to settle, and the clear water drawn off; the deposited starch is then stirred up with fresh water, and again allowed to subside, this process being repeated as long as the water is coloured, after which the starch is mixed up with a small quantity of water, and passed through a fine sieve to separate mechanically mixed impurities; it is finally drained and dried, first in a current of air, and afterwards by a gentle heat.

Starch cannot be extracted from wheat so easily as from potatoes, on account of the much larger proportion of other solid matters from which it must be separated.

To extract the starch, the coarsely ground wheat is moistened with water, and allowed to putrefy, as it easily does, in consequence of the alterable character of the gluten (which contains carbon, hydrogen, nitrogen, oxygen, and sulphur); the putrefying gluten excites fermentation in the sugar and part of the starch, producing acetic and lactic acids. These acids are capable of dissolving the remainder of the gluten, which may then be washed away by water, the subsequent processes being similar to those employed in the extraction of potato starch.

A far more economical and scientific method of extracting the starch consists in dissolving the gluten by means of a weak alkaline solution, which leaves the starch untouched, This process is especially applied in the manufacture of starch from rice (p. 735).

Arrowroot is the starch extracted from the root of the *Maranta arundinacea*, and of some other tropical plants.

In the preparation of tapioca and sago, the starch is dried at a temperature above 140° F., so that it loses its ordinary farinaceous appearance and becomes semi-transparent.

Sago is manufactured from the pith of certain species of palm, natives of the East Indian islands. The tree is split so as to expose the pith, which is mixed with water, and the starch, having been separated from the woody fibre in the usual manner, is pressed through a perforated metallic plate, which moulds it into small cylinders; these are placed in a revolving vessel and broken into rough spherical grains, which are steamed upon a sieve and dried.

Tapioca is obtained from the roots of the *Jatropha manihot*, a native of America. The roots are peeled and subjected to pressure, which squeezes out a juice employed by the Indians to poison their arrows, and containing a deleterious substance which has been named *jatrophine*. When the juice is allowed to stand it deposits starch, which is well washed, pressed through a colander, and dried at 212° F.

Oswego, or corn-flour, is the flour of Indian corn deprived of gluten by treatment with a weak solution of soda.

605. MALTING.—The tendency of starch to combine with the elements of water and pass into glucose (p. 733) is of immense importance in the chemistry of vegetation, as well as in that of food. It is, indeed, the chief chemical change concerned in the development of living from inanimate matter, being one of the first

processes involved in the germination of seed—the first step in the production of vegetables, which must precede the animals whose food they compose.

The components of all seeds are similar to those of wheat, which have been enumerated above; if the seeds be perfectly dried immediately after the removal from the parent plant, they may be preserved for a great length of time unchanged and without losing the power of germinating under favourable circumstances. The essential conditions of germination are the presence of air and moisture, and a certain temperature, which varies with the nature of the seed. These conditions being fulfilled, the seed absorbs oxygen from the air, and evolves carbonic acid gas, produced by the combination of the oxygen with the carbon of one or more of the most alterable constituents of the seed, such as the vegetable albumin or the gluten. This process of oxidation is attended with evolution of heat, which serves to maintain the seed at a degree of warmth most favourable to germination. The component particles of the albumin or gluten, having been set in motion by the action of the atmospheric oxygen, induce a movement or chemical change in the starch with which they are in contact, causing it to pass into dextrin and glucose, which, unlike the starch, are perfectly soluble in water, and capable of affording to the developing shoot the carbon, hydrogen, and oxygen which it requires for the increase of its frame. The production of glucose and of dextrin in germination is well illustrated by the sweet gummy character of the bread made from *sprouted* wheat, and is turned to practical account in the process of malting.

During the germination of all seeds there is formed, apparently by the oxidation of one of the more alterable constituents, a peculiar substance containing carbon, hydrogen, nitrogen, and oxygen, which has never yet been obtained from any other source, and is characterised by its remarkable property of inducing the conversion of starch into dextrin and grape-sugar. This substance has been termed *diastase* (διάστασις, *dissension*; *metaph. fermentation*), but has never yet been obtained in a state of sufficient purity to enable its formula to be satisfactorily determined. It may be extracted, however, from malt, by grinding it and mixing it with half its weight of warm water, which dissolves the diastase: the solution squeezed out of the malt is heated to about 179° F., filtered from any coagulated albumin, and mixed with absolute alcohol, which precipitates the diastase in white flakes. One part of diastase dissolved in water is capable of inducing the conversion of 2000* parts of starch into dextrin and grape-sugar, the diastase itself being exhausted in the process. A temperature of about 150° F. is most favourable to the action of diastase, which may be arrested entirely by raising the liquid to the boiling-point.

The great importance of diastase in the art of the brewer and distiller is at once apparent. In the process of *malting* barley, the grain is soaked in water, and afterwards spread out in thin layers upon the floor of a dark room (thus imitating the natural condition under which the seed germinates), which is maintained as nearly as possible at a constant and moderate temperature (between 55° and 62° F.); spring and autumn are, therefore, more favourable to malting than summer and winter. It soon evolves heat, and the grains begin to swell: in the course of twenty-four hours the germination commences, and the *radicle* makes its first appearance as a whitish protuberance; the grain is turned two or three times a day, in order to equalise the temperature. In about a fortnight the radicle has grown to about half an inch, by which time a sufficient quantity of diastase has been formed. In order to prevent the germination from proceeding further, the grain is killed by drying it at a temperature of 90° F. on perforated metallic plates, where it is afterwards heated to about 140° F., so as to render it brittle, after which it is sifted in order to separate the radicle, which is now easily broken off. This radicle is found to contain as much as $\frac{1}{5}$ of the total quantity of the nitrogen present in the barley, so that the *malt dust*, as the siftings are called, forms a valuable manure.

One hundred parts of barley generally yield about 80 parts of malt, but a part of the loss is due to water present in the barley, so that 100 parts of dry barley yield 90 parts of malt and 4 parts of malt dust, the difference, viz., 6 parts, representing the weight of the carbon converted into carbonic acid gas, of the hydrogen (if any) converted into water during the germination, and of soluble matters removed from the barley in steeping. Malt contains about $\frac{1}{125}$ of its

* 100,000, according to more modern authorities.

weight of diastase, far more than enough to ensure the conversion of the whole of its starch into sugar.

The following table illustrates the change in composition suffered by barley during the process of malting, leaving the moisture out of consideration :—

—	Barley.	After Steeping.	14½ Days on Floor.	Malt after Sifting.	Malt Dust.
Sugar . . .	2.56	1.56	12.14	11.01	11.35
Starch } Dextrin } . . .	80.42	81.12	70.09	72.03	43.68
Woody fibre . .	4.69	5.22	5.03	4.84	9.67
Albuminous matter .	9.03	9.83	10.39	9.95	26.90
Mineral matter . .	2.50	2.27	2.35	2.17	8.40
	100.00	100.00	100.00	100.00	100.00

BREWING.

606. In order to prepare beer, the brewer *mashes* the ground malt with water at about 180° F., for some hours, when the diastase induces the conversion, into dextrin and sugar, of the greater part of the starch which has not been so changed during the germination, and the *wort* is ready to be drawn off for conversion into beer. The undissolved portion of the malt, or *brewers' grains*, still contains a considerable quantity of starch and nitrogenised matter, and is employed for feeding pigs.

That malt contains far more diastase than is necessary to convert its starch into sugar, is shown by adding a little infusion of malt to the viscid solution of starch, and maintaining it at about 150° F. for a few hours, when the mixture will have become far more fluid, and will no longer be coloured blue by solution of iodine. In distilleries, advantage is taken of the excess of diastase in malt, by adding three or four parts of unmalted grain to it, when the whole of the starch in this latter is also converted into dextrin and sugar, and the labour and expense of malting it are avoided.

The wort obtained by infusing malt in water contains not only glucose, dextrin, and diastase, but a considerable quantity of nitrogenised matter formed from the gluten (or albuminous matter) of the barley. Before subjecting it to fermentation it is boiled with a quantity of hops, usually amounting to about $\frac{1}{400}$ of the weight of the malt employed, which is found to prevent, in great measure, the tendency of the beer to become sour in consequence of the conversion of the alcohol into acetic acid.

The *hop* contains about 10 per cent. of an aromatic yellow powder called *lupulin*, which appears to be the active portion, and contains a volatile oil of peculiar odour, together with a very bitter substance.

The hopped wort is run off into a vat, where it is allowed to deposit the undissolved portion of the hops, and the clear liquor is drawn off into shallow coolers, where its temperature is lowered as rapidly as possible to about 60° F., the cooling being usually hastened by cold water circulating through pipes which traverse the coolers. If the wort be cooled too slowly, the nitrogenised matter which it contains undergoes an alteration by the action of the air, in consequence of which the beer is very liable to become acid.

The wort is now transferred to the *fermenting tun*, where it is made to ferment by the addition of yeast, usually in the proportion of $\frac{1}{10}$ of its volume.

Yeast has been depicted and described at p. 562.

The yeast cells contain a substance somewhat resembling albumin enclosed in a thin membrane, the composition of which is similar to that of cellulose. They also contain a peculiar nitrogenised body (*invertase*) resembling diastase, and capable of inducing the conversion of cane-sugar ($C_{12}H_{22}O_{11}$) into glucose ($C_6H_{12}O_6$). Accordingly, when yeast is added to a solution of cane-sugar the liquid is found

to increase in specific gravity (a solution of cane-sugar having a lower density than one containing an equivalent quantity of glucose) previously to the commencement of fermentation, and the application of tests readily proves the presence of glucose in the solution.

The glucose then undergoes the decomposition known as *alcoholic fermentation*, described at p. 562.

During the fermentation, the yeast cells are gradually broken up, so that a given quantity of yeast is capable of fermenting only a limited quantity of sugar. On an average a quantity of yeast containing between two and three parts of solid matter is required to complete the fermentation of 100 parts of sugar. The solution remaining after the fermentation is found to contain salts of ammonium, which have been formed at the expense of the nitrogen of the yeast.

If the liquid in which the yeast excites fermentation contains nitrogenised matters and phosphates, the yeast-plant grows, and its quantity increases; thus in the sweet wort from malt, the yeast is nourished by the altered gluten and by the phosphates, so that it increases to six or eight times its original weight.

If yeast be heated to the boiling-point of water, the plant is killed, as might be expected, and loses its power of inducing alcoholic fermentation; but it may be dried at a low temperature, or by pressure, without losing its fermenting power, and *dried yeast* is an article of commerce. German dried yeast is produced in the fermentation of rye for making Hollands.

In the fermentation of beer, the yeast is carried up to the surface by the effervescence due to the escape of the carbonic acid gas, and is eventually removed, in order to be employed for the fermentation of fresh quantities of wort. When the fermentation has proceeded to the required extent, the beer is stored for consumption.

It will be seen that the chief constituents of beer are the alcohol, the nitrogenised substance derived from the albuminous matter of the barley and not consumed in the growth of the yeast, the unaltered glucose and dextrin, the brown or yellow colouring-matter formed during the fermentation, the essential oil and bitter principle of the hop.

Beer also contains acetic acid (formed by the oxidation of the alcohol, p. 590), free carbonic acid, which gives it its sparkling character, together with the lactic and succinic acids and glycerine, formed as secondary products of the fermentation, and ammoniacal salts derived from the yeast. The soluble mineral substances from the barley are also present, *minus* the phosphates abstracted by the yeast.

The proportions of the constituents of course vary greatly, as will be seen from the following examples:—

Percentage.	Allsopp's Ale.	Bass's Ale.	Strong Ale.	Whitbread's Porter.	Whitbread's Stout.
Alcohol . . .	6.00	7.00	8.65	4.20	6.00
Acetic acid . .	0.20	0.18	0.12	0.19	0.18
Sugar and other solid matters	5.00	4.80	6.60	5.40	6.38

The dark colour of porter and stout is caused by the addition of a quantity of *high-dried malt* which has been exposed to so high a temperature in the kiln as to convert a portion of its sugar into a dark brown soluble substance called *caramel*. The peculiar aroma of beer is probably due to the presence of acetic ether, produced during the fermentation.

In some cases, when the operation of brewing has been badly conducted, the beer becomes *ropy*, or undergoes the *viscous fermentation*. In this case the glucose suffers a peculiar transformation, resulting in the production of a mucilaginous substance resembling gum in its composition. This change may be induced by yeast which has been boiled, or by water in which flour or rice has been steeped. During this viscous fermentation a part of the glucose is often converted into mannite ($C_6H_{14}O_6$).

WINES AND SPIRITS.

607. Wine is essentially composed of 8 or 10 parts of alcohol, with 85 or 90 of water, together with minute quantities of certain fragrant ethers, of colouring-matter, of potassium bitartrate, and of the mineral substances derived from the grape-juice. Glycerine and succinic acid are also found in wines, being secondary products of the alcoholic fermentation.

Those wines in which the whole of the sugar has been fermented are known as *dry* wines; whilst *fruity* wines still retain a considerable quantity of sugar.

The preparation of wines differs from that of beer in the circumstance that no addition of ferment is necessary, the fermentation being spontaneous. Grape-juice contains, in addition to grape-sugar, vegetable albumin, potassium tartrate, and the usual mineral salts found in vegetable juices. The husks, seeds, and stalks of the grape contain a considerable quantity of tannin, together with certain blue, red, and yellow colouring-matters.

When the expressed juice remains for a short time in contact with the air, the germs or spores of yeast (p. 562) which float in the air are deposited on the surface of the juice, at the expense of which they begin to grow, exciting the vinous fermentation in the sugar, and a scum of yeast is formed upon the surface. If this fermentation takes place in contact with the husks of the dark grapes, the alcohol dissolves the colouring-matter, and a red wine results; whilst for the production of white wines, the husks, &c., are separated previously to the fermentation, and the juice is exposed as little as possible to the air.

White wines are rather liable to become *ropy* from viscous fermentation, but this is prevented by the addition of a small quantity of tannin, which precipitates the peculiar ferment. The tannin for this purpose is extracted from the husks and stalks of the grapes themselves, and already exists in red wine.

Red wines, such as port and claret, are often very astringent from the tannin dissolved out of the husks, &c., during the fermentation. Port wine, when freshly bottled, still retains in solution a considerable quantity of acid potassium tartrate or bitartrate of potash ($KHC_4H_4O_6$), but after it has been kept some time, and become more strongly alcoholic, this salt is deposited, together with a quantity of the colouring-matter, in the form of a crust upon the side of the bottle. Thus a dark, *fruity* port becomes *tawny* and *dry* when kept for a sufficient length of time, the sugar having been converted into alcohol.

When the wine contains an excess of tartaric acid, it is customary to add to it some neutral potassium tartrate ($K_2C_4H_4O_6$), which precipitates the acid in the form of bitartrate.

The preparation of champagne is conducted with the greatest care. The juice or *must* is carefully separated from the *marc* or husks, and is often mixed with 1 per cent. of brandy before fermentation. After about two months the wine is drawn off into another cask, and clarified with isinglass dissolved in white wine, and added in the proportion of about half an ounce to 40 gallons. This combines with the tannin to form an insoluble precipitate, which carries with it any impurities floating in the wine. After another interval of two months, the wine is again drawn off, and a second clarification occurs; and in two months more the wine is drawn off into bottles containing a small quantity of pure sugar-candy dissolved in white wine. The bottles, having been securely corked and wired, are laid down upon their sides for eight or ten months, during which time the fermentation of the newly added sugar happens, and the carbonic acid produced dissolves in the wine, whilst a quantity of yeast is separated. In order to render the wine perfectly clear, the bottle is left for about three weeks in such a position that the deposit may subside into the neck against the cork, which is then unwired so that the pressure of the accumulated carbonic acid gas may force it out together with the deposit; the bottle, having been rapidly filled up with white wine, is again corked, wired, covered with tinfoil, and sent into the market. Pink champagne is prepared from the must which is squeezed out of the marc after it has ceased to run freely, and contains a little of the colouring-matter of the husk. The colour is also sometimes imparted by adding a little tincture of litmus.

The proportion of alcohol in wines varies greatly, as will be seen from the following statement of the weight of alcohol in 100 parts of the wine:—

Port	15 to 17	Claret	8 to 9
Sherry . . .	14 to 16	Rudesheimer . .	7 to 8.5
Champagne . .	11.5		

Sherry contains from 1 to 5 per cent. of sugar, port from 3 to 7 per cent., and Tokay 17 per cent.; in the last case the sugar is increased by adding some of the must, concentrated by evaporation, to the wine, previously to bottling.

The *bouquet* or fragrance of wine is due to the presence of certain fragrant ethers (*ethereal salts*), especially of œnanthic, pelargonic and acetic ether, formed during the fermentation or during the subsequent storing of the wine. It is to the increased quantity of such fragrant ether that the superior bouquet of many old wines is due.

Distilled spirits.—The varieties of ardent spirits are obtained from fermented liquids by distillation, so that they consist essentially of alcohol more or less diluted with water, and flavoured either with some of the volatile products of the fermentation, or with some essential oil added for the purpose.

Brandy is distilled from wine, and coloured to the required extent with burnt sugar (caramel). Its flavour is due chiefly to the presence of œnanthic ether derived from the wine. The colour of genuine pale brandy is due to its having remained so long in the cask as to have dissolved a portion of brown colouring-matter from the wood, and is therefore an indication of its age. Hence arose the custom of adding caramel, and sometimes infusion of tea, to impart the colour and astringency due to the tannin dissolved from the wood by old brandy.

Whiskey is distilled from fermented malt which has been dried over a peat fire, to which the characteristic smoky flavour is due.

Gin is also prepared from fermented malt or other grain, and is flavoured with the essential oil of juniper, derived from juniper berries added during the distillation.

Rum is distilled from fermented molasses, and appears to owe its flavour to the presence of butyric ether, or of some similar compound.

Arrack is the spirit obtained from fermented rice.

Kirschwasser and *maraschino* are distilled from cherries and their stones, which have been crushed and fermented.

Some varieties of British brandy and whiskey are distilled from fermented potatoes, or from a mixture of potatoes and grain, when there distils over, together with ordinary alcohol, especially towards the end of the distillation, another spirit belonging to the same class, but distinguished from alcohol by its nauseous and irritating odour. This substance, which is known as *potato-spirit, amylic alcohol*, or *fusel oil* ($C_5H_{12}O$), also occurs, though in very minute quantity, in genuine wine brandy. The manufacturers of spirit from grain and potatoes remove a considerable part of this disagreeable and unwholesome substance by leaving the spirit for some time in contact with wood-charcoal.

BREAD.

608. The chemistry of fermentation is intimately connected with the ordinary process of bread-making. It will be remembered that wheaten flour (p. 803) consists, essentially, of starch and gluten, with a little dextrin and sugar. On mixing the flour with a little water, it yields a *dough*, the tenacity of which is due to the gluten present in the flour. If this dough be tied up in a piece of fine muslin, and kneaded under a stream of water, the starch will be suspended in the water, and will pass through the muslin, whilst the gluten will remain as a very tough elastic mass, which speedily putrefies if exposed to the air in a moist state, and dries up to a brittle horny mass at the temperature of boiling water.

On analysis, gluten is found to contain carbon, hydrogen, nitrogen, and oxygen, in proportions which may be represented by the empirical formula $C_{24}H_{30}N_6O_7$, though it cannot be regarded as a single independent substance, but as a mixture of three substances very closely allied in composition.

When gluten is boiled with alcohol, one portion refuses to dissolve, and has been named *vegetable fibrin*, from its resemblance to the substance forming the muscles of animals. When the solution in alcohol is allowed to cool, it deposits a white flocculent matter, very similar to the *casein* which composes the curd of milk. On adding water to the cold alcoholic solution, a third substance

(*glutin*) is separated, which much resembles the albumin found so abundantly in the blood.

The presence in gluten of three substances, similar to the three principal components of the animal body, leads us to form a high opinion of its value as a nutritive compound. But gluten itself, separated from the flour by the process above described, would be found very difficult of digestion, on account of its resistance to the solvent action of the fluids in the stomach; indeed, the dough composed of flour and water is proverbially indigestible even when baked. In order to make it fit for food, it must be rendered spongy or porous, so as to expose a larger surface to the action of the digestive fluids of the body; the most direct method of effecting this is the one adopted in the manufacture of the *aerated bread*, and consists in mixing the flour with water which has been highly charged, under pressure, with carbonic acid gas; the mixing having been effected in a strong closed iron vessel, an aperture in the lower part of this is opened, when the pressure of the accumulated gas forces the dough out into the air, and the gas which has been imprisoned in the dough expands, conferring great porosity and sponginess upon the mass in its attempt to escape. In another process for preparing *unfermented bread*, the flour is mixed with a little bicarbonate of soda, and is then made into a dough with water acidified with hydrochloric acid; the latter, decomposing the bicarbonate of soda, liberates carbonic acid gas, which renders the bread porous. The sodium chloride formed at the same time remains in the bread. In the preparation of cakes and pastry, the same object is sometimes attained by adding carbonate of ammonia to the dough; when heat is applied in the baking, the salt is converted into vapour which distends the dough.

In the common process of bread-making, however, the carbonic acid gas destined to confer sponginess upon the dough is evolved by the fermentation of the sugar contained in the flour; the latter having been kneaded with the proper proportion (usually about half its weight) of water, a little yeast and salt are added, and the mixture is allowed to stand at a temperature of about 70° F. for some hours. The dough swells or *rises* considerably in consequence of the escape of carbonic acid gas, the sugar being decomposed into that gas and alcohol, as in ordinary fermentation. The spongy dough is then baked in an oven, heated to about 500° F., when a portion of the water and the whole of the alcohol are expelled, the carbonic acid gas being also much expanded by the heat, and the porosity of the bread increased. The granules of starch are much altered by the heat, and become far more digestible. Although the temperature of the inside of the loaf does not exceed 212° F., the outer portion becomes torrefied or scorched into crust.

Occasionally, instead of yeast, *leaven* is employed, in order to ferment the sugar, leaven being dough which has been left in a warm place until decomposition has commenced.

The passage of new into stale bread does not depend, as was formerly supposed, upon the drying of the bread consequent upon its exposure to air, but it is a true molecular transformation which occurs equally well in an air-tight vessel, and without any loss of weight. It is well known that when a thick slice of stale bread is toasted, which *dries* it still further, the crumb again becomes soft and spongy as in new bread; and if a stale loaf be again placed in the oven, it is entirely reconverted into new bread.

Wheaten flour is particularly well fitted for the preparation of bread on account of the great tenacity of its gluten. Next to wheat in this respect stands rye, whilst the other cereals contain a gluten so deficient in tenacity that it is impossible to convert them into good bread.

Barley bread is close and heavy, since its nitrogenised matter is chiefly present in the form of albumin, which does not vesiculate like gluten during the fermentation. Even in wheaten flour the tenacity of the gluten is liable to variation, and in order to obtain good bread from a flour the gluten of which is inferior in this respect, it is customary to employ a minute proportion of alum. This addition being considered unwholesome by some persons, it would be better to substitute lime-water, which has been found by Liebig to have a similar effect. Sulphate of copper improves in a very striking manner the quality of the bread prepared from inferior flour, but this salt is far more objectionable than alum.

TEA, COFFEE, ETC.

609. A very remarkable instance of the application of chemistry to explain the use of widely different articles of diet by different nations, with a view to the production of certain analogous effects upon the system, is seen in the case of coffee, tea, Paraguay tea, and the *kola nut* (of Central Africa), which are very dissimilar in their sensible properties, and afford little or no gratification to the palate, owing what attractions they possess chiefly to the presence, in each, of one and the same active principle or alkaloid, which has a special effect upon the animal economy. This alkaloid is known as caffeine or theine, and is associated, in the three articles of diet mentioned above, with various substances, which give rise to their diversity in flavour.

The raw coffee-berry presents, on the average, the following composition :—

100 *parts of Raw Coffee contain*—

Woody fibre	34.0
Water	12.0
Fat	12.0
Sugar and gum	15.5
Legumin, or some allied substance	13.0
Caffeine	1.5
Caffeic acid	4.0
Mineral substances	7.0

When the raw berry is treated with hot water, the infusion, which contains the sugar and gum, the legumin, caffeine, and *caffeic acid* ($C_9H_8O_4$), has none of the peculiar fragrance which distinguishes the ordinary beverage, and is due to an aromatic volatile oily substance termed *caffeol* ($C_8H_{10}O_2$) formed during the roasting to which the berry is subjected before use. This volatile oil, which is present in very minute quantity, is produced from one of the soluble constituents of the berry (probably from the caffeic acid), for if the infusion of raw coffee be evaporated to dryness, the residue, when heated, acquires the characteristic odour of roasted coffee.

Acetic and palmitic acids are also found among the products of coffee-roasting.

The roasting is effected in ovens at a temperature rather below 400° F., when the berry swells greatly, and loses about ¼ of its weight, becoming brittle, and easily ground to powder. It also becomes very much darker in colour, from the conversion of the greater part of its sugar into caramel (p. 732), which imparts the dark brown colour to the infusion of coffee. If the roasting be carried too far, a very disagreeable flavour is imparted to the coffee, by the action of heat upon the legumin and other nitrogenised substances contained in the berry.

From 100 parts of the roasted coffee, boiling water extracts about 20 parts, consisting of caffeine, caffeic acid, caramel, legumin, a little suspended fatty matter, fragrant volatile oil (caffeone), and salts of potassium (especially the phosphate). The undissolved portion of the coffee contains, beside the woody fibre, a considerable quantity of nitrogenised (and nutritious) matter, and hence the custom, in some countries, of taking this residue together with the infusion.

The constituents of the leaves of the tea-plant (*Thea sinensis*) exhibit a general similarity to those of the coffee-berry. In the fresh leaf we find, in addition to the woody fibre, a large quantity of a substance containing nitrogen, similar to legumin, an astringent acid similar to tannic acid, a small quantity of caffeine, and some mineral constituents.

The aroma of tea does not belong to the fresh leaf, but is produced, like that of coffee, during the process of drying by heat, which develops a small quantity of a peculiar volatile oil, having powerful stimulating properties. The freshly dried leaf is comparatively so rich in this oil that it is not deemed advisable to use it until it has been kept for some time.

Green and black tea are the produce of the same plant, the difference being caused by the mode of preparation. For green tea the leaves are dried over a fire as soon as they are gathered, whilst those intended for black tea are allowed to remain exposed to the air in heaps for several hours, and are then rolled with the hands and partially dried over a fire, these processes being repeated three or four times to develop the desired flavour. The black colour appears to be due to the action of the air upon the tannin present in the leaf.

Boiling water extracts about 30 parts of soluble matter from 100 of black tea, and 36 from 100 of green tea. The principal constituents of the infusion of tea are tannin, aromatic oil, of which green tea contains about 0.8 and black tea 0.6 per cent., and caffeine, the proportion of which, in the dried leaf, varies from 2.2 to 4.1 per cent., being present in larger quantity in green tea.

The spent leaves contain the greater part of the legumin and a considerable quantity of caffeine, which may be extracted by boiling them with water, and treating the decoction as at p. 775.

Cocoa and *chocolate* are prepared from the cacao-nut, which is the seed of *Theobroma cacao*, and is characterised by the presence of more than half of its weight (*minus* the husk) of a fatty substance known as *cacao-butter*, and consisting of olein and stearin, which does not become rancid like the natural fats generally. The cacao-nut also contains a large quantity of starch, a nitrogenised substance resembling gluten, together with gum, sugar and *theobromine*, a feeble base very similar to caffeine, but having the composition $C_7H_8N_4O_2$.

The seeds are allowed to ferment in heaps for a short time, which improves their flavour, dried in the sun and roasted like coffee, which develops the peculiar aroma of cocoa. The roasted beans having been crushed and winnowed to separate the husks, are ground in warm mills, in which the fatty matter melts and unites with the ground beans to a paste, which is mixed with sugar and pressed into moulds. In the preparation of chocolate, vanilla and spices are also added.

From the composition of cocoa and chocolate it is seen that, when consumed, as is usual, in the form of a paste, they would prove far more nutritious than mere infusions of tea and coffee.

ANIMAL CHEMISTRY.

610. Our acquaintance with the chemistry of the substances composing the bodies of animals is still very limited, although the attention of many accomplished investigators has been directed to this branch of the science. The reasons for this are to be found, first, in the susceptibility to change exhibited by animal substances when removed from the influence of life; and secondly, in the absence, in such substances, of certain physical properties by which we might be enabled to separate them from other bodies with which they are associated, and to verify their purity when obtained in a separate state. Two of the most important of these properties are volatility and the tendency to crystallise. When a substance can suffer distillation without change, it will be remembered that its boiling-point affords a criterion of its purity; or if it be capable of crystallising, this may be taken advantage of in separating it from other substances which crystallise more or less easily than itself, and its purity may be ascertained from the absence of crystals of any other form than that belonging to the substance. But the greater number of the components of animal frames can neither be crystallised nor distilled, so that many of the analyses which have been made of such substances differ widely from each other, because the analyst could never be sure of the perfect purity of his material; and even when concordant results have been obtained as to the percentage composition of the substance, the formula deduced from it has been of so singular and exceptional a character as to cast very strong suspicion upon the purity of the substance.

Accordingly, the chemical formulæ of a great many animal substances are perfectly unintelligible, conveying not the least information as to the position in which the compound stands with respect to other substances, or the changes which it might undergo under given circumstances.

Animal chemistry is, for the above reasons, in a very backward condition, as compared with vegetable and mineral chemistry, though an observation of the progress of research affords us the consolation, that a steady advance is being made towards a generalisation of the facts which have been discovered, especially by deductive reasoning from those two other departments of the science.

611. **Milk.**—The chemistry of milk is well adapted to introduce the study of animal chemistry, because that liquid contains representatives of all the substances which make up the animal frame; and it is on this account that it occupies so high a position among articles of food.

Although, to the unaided eye, milk appears to be a perfectly homogeneous fluid, the microscope reveals the presence of innumerable globules floating in a transparent liquid, which is thus rendered opaque. If milk be very violently

agitated for several hours, masses of an oily fat (butter, p. 799) are separated from it, and leave the liquid transparent. This fat was originally distributed throughout the milk, in minute globules, which were made to coalesce by the violent agitation.

For the preparation of butter, it is usual to allow the milk to stand for some hours, when a layer of *cream* collects upon the surface, the proportion of which is very variable, but is generally about $\frac{1}{10}$ of the volume of the milk.* The *skimmed milk* retains about half of the fatty matter. This cream contains about 35 per cent. (by weight) of fat, 3 per cent. of casein, and water. When the cream is *churned*, the fat globules are broken, and the fat unites into a semi-solid mass of butter, from which the butter-milk containing the casein may be separated. If this be not done effectually, the casein which is left in the butter, being a nitrogenised substance, will soon begin to decompose, and will induce a decomposition in the butter (p. 799), resulting in the formation of certain volatile acids, which impart to it a rancid and offensive taste and odour. To prevent this, salt is generally added to butter which has been less carefully prepared in order to preserve the casein from decomposition. *Butter-milk* contains about one-fourth of the fatty matter of the milk.

Pure butter is essentially a mixture of stearin, palmitin and olein with smaller quantities of other fats, such as butyrin, caprin, and caproin (p. 799).

Fresh milk is slightly alkaline to test-papers, but after a short time it acquires an acid reaction; and if it be then heated, it coagulates from the separation of the casein. This spontaneous acidification of milk is caused by the fermentation of the *sugar of milk*, which results in the production of *lactic acid*.

If milk be maintained at a temperature of about 90° F., the fermentation results in the production of alcohol and carbonic acid, for although milk-sugar is not fermented like ordinary sugar, by contact with yeast, it appears, under the influence of the changing casein at a favourable temperature, to be converted first into grape-sugar (p. 726), and afterwards into alcohol and carbonic acid. The Tartars prepare an intoxicating liquid, which they call *koumiss*, by the fermentation of milk.

When an acid is added to milk, the casein is separated in the form of curd, in consequence of the neutralisation of the soda which retains it dissolved in fresh milk, and this curd carries with it, mechanically, the fat globules of the milk, leaving a clear yellow *whey*.

In the preparation of *cheese*, the milk is coagulated by means of *rennet*, which is prepared from the lining membrane of a calf's stomach. This is left in contact with the warm milk for some hours, until the coagulation is completed. The curd is collected and pressed into cheeses, which are allowed to ripen in a cool place, where they are occasionally sprinkled with salt. The peculiar flavour which the cheese thus acquires is due to the decomposition of the casein, giving rise to the production of certain volatile acids, such as butyric, valerianic, and caproic, which have very powerful and characteristic odours. If this ripening be allowed to proceed very far, ammonia is developed by the putrefaction of the casein, and in some cases the ethers of the above-mentioned acids are produced, at the expense probably of a little sugar of milk left in the cheese, conferring the peculiar aroma perceptible in some varieties of it.

The different kinds of cheese are dependent upon the kind of milk used in their preparation, the richer cheeses being, of course, obtained from milk containing a large proportion of cream; such cheese fuses at a moderate heat, and makes good toasted cheese, whilst that which contains little butter never fuses completely, but dries and shrivels like leather. Double Gloucester and Stilton are made from a mixture of new milk and cream; Cheddar cheese is made from new milk alone; Cheshire and American cheeses from milk robbed of about one-eighth of its cream; Dutch cheese and the *Skim Dick* of the midland counties, from skimmed milk.

The characteristic constituents of milk are the casein and milk-sugar, but the proportions in which these are present vary widely not only with the animal from which the milk is obtained, but with the food and condition of the animal. A general notion of their relative quantities, however, may be gathered from the following table:—

* The separation of cream is now effected, in large dairies, by means of a *centrifugal separator*, making several thousand revolutions per minute.

	Cow.	Ass.	Goat.	Woman.
Water	87.2	89.6	85.7	87.4
Fat	3.7	1.7	4.8	3.8
Casein	3.0	0.7	3.2	1.0
Albumin . . .	0.5	1.5	1.1	1.3
Milk-sugar . . .	4.9	6.0	4.5	6.2
Mineral salts . . .	0.7	0.5	0.7	0.3

The soluble salts present in milk include the phosphates and chlorides of potassium and sodium, whilst the insoluble salts are the phosphates of calcium, magnesium, and iron. All these salts are in great request for the nourishment of the animal frame.

The milk supplied to consumers living in towns is subject to considerable adulteration; but in most cases this is effected by simply removing the cream and diluting the skimmed milk with water, a fraud which is not easily detected, as might be supposed, by determining the specific gravity of the milk, for since milk is heavier than water (1.032 sp. gr.), and the fatty matter composing cream is lighter than water, a certain quantity of cream might be removed, and water added, without altering the specific gravity of the milk.

The simplest method of ascertaining the quality of the milk consists in setting it aside for twenty-four hours in a tall narrow tube (*lactometer* or *creamometer*) divided into 100 equal parts, and measuring the proportion of cream which separates, this averaging, in pure milk, from eleven to thirteen divisions. The measurement of the cream is effected in fifty minutes by using a *centrifugal separator*, in which the tube containing the milk is placed in a case attached to a centrifugal apparatus making 1200 revolutions per minute. By shaking milk with a little potash and ether, the butter may be dissolved in the ether which rises to the surface, and if this be poured off and allowed to evaporate, the weight of the butter may be ascertained; or the milk may be evaporated by a steam heat, and the fat dissolved by treating the residue with ether. The amount of fat is sometimes found by taking the specific gravity of the ethereal solution, and referring to a table giving the corresponding quantity of fat. One thousand grains of milk should give, at least, 27 or 28 grains of butter. Since, however, the milk of the same cow gives very different quantities of cream at different times, it is difficult to state confidently that adulteration has been practised. The standard usually adopted by analysts is 25 grains of fat or butter and 90 grains of "solids not fat" in 1000 grains of milk.

612. **Blood.**—The blood, from which the various organs of the body directly receive their nourishment, is the most important, as well as the most complex, of the animal fluids. Its chemical examination is attended with much difficulty, on account of the rapidity with which it changes after removal from the body of the animal.

On examining freshly drawn blood under the microscope, it is observed to present some resemblance to milk in its physical constitution, consisting of opaque flattened globules floating in a transparent liquid; the globules, in the case of blood, having a well-marked red colour.

In a few minutes after the blood has been drawn, it begins to assume a gelatinous appearance, and the semi-solid mass thus formed separates into a red solid portion or *clot*, which continues to shrink for ten or twelve hours, and a clear yellow liquid or *serum*. It might be supposed that this coagulation is due to the cooling of the blood, but it is found by experiment to take place even more rapidly when the temperature of the blood is raised one or two degrees after it has been drawn; and, on the other hand, if it be artificially cooled, its coagulation is retarded. Indeed, the reason for this remarkable behaviour of the blood is not yet understood.

If the coagulum or clot of blood be cut into slices, tied in a cloth, and well washed in a stream of water, the latter runs off with a bright red colour, and a tough yellow filamentous substance is left upon the cloth; this substance is called *fibrin*, and its presence is the proximate cause of the coagulation of the blood, for if the fresh blood be well whipped with a bundle of twigs or glass rods, the

fibrin will adhere to them in yellow strings, and the *defibrinated* blood will no longer coagulate on standing. If this blood, from which the fibrin has been extracted, be mixed with a large quantity of a saline solution (for example, 8 times its bulk of a saturated solution of sodium sulphate), and allowed to stand, the red globules subside to the bottom of the vessel.

These globules are minute bags of red fluid, enclosed in a very thin membrane or *cell-wall*, and if water were mixed with the defibrinated blood, since its specific gravity is lower than that of the fluid in the globules, it would pass through the membrane (by *osmosis*), and so swell the latter as to break it and disperse the contents through the liquid.

The red fluid contained in these blood globules consists of an aqueous solution, containing as its principal constituents a substance known as *globulin*, which very nearly resembles albumin, and the peculiar colouring-matter of the blood, which is called *hæmatin*.

Beside these, the globules contain a little fatty matter and certain mineral constituents, especially the iron (which is associated in some unknown form with the colouring-matter), the chlorides of sodium and potassium, and the phosphates of potassium, sodium, calcium, and magnesium.

Though the quantities of these constituents are not invariable, even in the same individual, the following numbers may be taken as representing the average composition of these globules:—

1000 *parts of Blood Globules contain*—

Water	688.00	Organic substances of unknown nature	2.60
Globulin	282.22		
Hæmatin	16.75	Mineral substances *	8.12
Fat	2.31		

The Mineral Substances consist of

Potassium	3.328	Oxygen	0.667
Phosphoric oxide (P_2O_5)	1.134	Calcium phosphate	0.114
Sodium	1.052	Magnesium phosphate	0.073
Chlorine	1.686	Sulphuric oxide (SO_3)	0.066

The liquid in which the blood globules float is an alkaline solution containing albumin, fibrin and saline matters in about the proportions here indicated.

1000 *parts of Liquor Sanguinis contain*—

Water	902.90	Organic substances of unknown nature	3.94
Albumin	78.84		
Fibrin	4.05	Mineral substances	8.55
Fat	1.72		

The Mineral Substances consist of—

Sodium	3.341	Phosphoric oxide (P_2O_5)	0.191
Chlorine	3.644	Sulphuric oxide (SO_3)	0.115
Potassium	0.323	Calcium phosphate	0.311
Oxygen	0 403	Magnesium phosphate	0.222

The alkaline character of this liquid appears to be due to the presence of carbonate and phosphate of sodium.

613. **Flesh.**—The fibrin composing muscular flesh contains about three-fourths of its weight of water, a part of which is due to the blood contained in the vessels traversing it, and another part to the *juice of flesh*, which may be squeezed out of the chopped flesh. In this juice of flesh there are certain substances which appear to play a very important part in nutrition. The liquid is distinctly acid, which is remarkable when the alkaline character of the blood is considered, and contains phosphoric, lactic, and butyric acid, together with creatine (p. 676), inosite (p. 716), and saline matters. By soaking minced flesh in cold water and well squeezing it in a cloth, a red fluid is obtained containing the juice of flesh mixed with a little blood.

The saline constituents of the juice of flesh are chiefly phosphates of potassium and magnesium, with a little chloride of sodium. It is worthy of notice that potassium is the predominant alkali-metal in the juice of flesh, whilst sodium predominates in the blood, especially in the serum.

* Exclusive of the iron which is associated with the hæmatin.

According to Liebig, the acidity of the juice of flesh is chiefly due to the acid phosphate of potassium, KH_2PO_4, whilst the alkalinity of the blood is caused by sodium phosphate, Na_2HPO_4; and it has been suggested that the electric currents which have been traced in the muscular fibres are due to the mutual action between the acid juice of flesh and the alkaline blood, separated only by thin membranes from each other, and from the substance of the muscles and nerves.

The average composition of flesh may be represented as follows:—

Water	78
Fibrin, vessels, nerves, cells, &c.	17
Albumin	2.5
Other constituents of the juice of flesh	2.5
	100.0

Liebig's extract of meat is prepared by exhausting all the soluble matters from the flesh with cold water, separating the albumin by coagulation and evaporating the liquid at a steam heat to a soft extract. It contains about half its weight of water, 40 per cent. of the organic constituents of the juice of flesh (albumin excepted), and 10 per cent. of saline matter.

Cooking of meat.—A knowledge of the composition of the juice of flesh explains the practice adopted, in boiling meat, of immersing it at once in boiling water, instead of placing it in cold water, which is afterwards raised to the boiling-point. In the latter case, the water would soak into the meat, and remove the important nutritive matter contained in the juice; whilst, in the former, the albumin in the external layer of flesh is at once coagulated, and the water is prevented from penetrating to the interior. In making soup, of course, the opposite method should be followed, the meat being placed in cold water, the temperature of which is gradually raised, so that all the juice of flesh may be extracted and the muscular fibre and vessels alone left.

The object to be attained in the preparation of *beef-tea* is the extraction of the whole of the soluble matters from the flesh, to effect which the meat should be minced as finely as possible, soaked for a short time in an equal weight of cold water, and slowly raised to the boiling-point, at which it is maintained for a few minutes. The liquid strained from the residual fibrin contains all the constituents of the juice except the albumin, which has been coagulated.

When meat is roasted, the internal portions do not generally attain a sufficiently high temperature to coagulate the albumin of the juice, but the outside is heated far above 212° F.; so that the meat becomes impregnated to a greater extent with the melted fat, and some of the constituents of the juice in this part suffer a change, which gives rise to the peculiar flavour of roast meat. The brown sapid substance thus produced has been called *osmazome*, but nothing is really known of its true nature. In salting meat, for the purpose of preserving it, a great deal of the juice of flesh oozes out, and a proportionate loss of nutritive matter is sustained.

614. **Urine** always contains a large proportion of alkaline and earthy salts, especially of sodium chloride, phosphate and sulphate of potassium, and phosphates of calcium, magnesium, and ammonium.

The average composition of human urine may be thus stated:—

Water	956.80
Urea	14.23
Uric acid	0.37
Mucus	0.16
Hippuric acid, creatinine, ammonia, colouring-matter, and unknown organic matters	15.03
Chloride of sodium	7.22
Phosphoric oxide (P_2O_5)	2.12
Potash	1.93
Sulphuric oxide (SO_3)	1.70
Lime	0.21
Magnesia	0.12
Soda	0.05
	999.94

CHEMISTRY OF VEGETATION.

615. Comparatively few of the elements enter into the composition of plants, and of those that do so only ten are, according to our present knowledge, absolutely essential to the growth of the plants; these are carbon, hydrogen, oxygen, nitrogen, sulphur, phosphorus, potassium, calcium, magnesium, and for plants containing chlorophyll, iron. At the same time sodium, silicon, and chlorine are invariably present, while manganese, fluorine, and minute quantities of other elements are generally to be found.

The carbon, hydrogen, and oxygen occur in all the organic constituents of the plant. The nitrogen occurs in the albuminoids, together with a small quantity of the sulphur; also in the amides, alkaloids, and nitrates. The metals occur as phosphates, nitrates, sulphates, and vegetable salts—chiefly oxalates, malates, tartrates, and citrates.

The carbon is derived by green plants from the carbon dioxide of the air, while plants destitute of chlorophyll are capable of deriving carbon from organic matter in the soil. The hydrogen and oxygen are derived from the water of the soil.

The source from which the plant derives its nitrogen has long been a subject of discussion. This element, as it exists uncombined in the air, is not absorbed by the plant to any appreciable extent, if at all; and the small quantities of ammonia and nitric acid in the air are quite inadequate to furnish the necessary supply for any extensive growth. The conclusion is that the nitrogen must be derived from the soil, and the beneficial effect of manuring with nitrates and ammonium salts supports this view. That nitrates are absorbed in solution by plant roots is certain, and nitrates are always fairly abundant in a fertile soil during the growing season, being produced by the nitrification (p. 87) of the ammonia derived from decaying vegetable matter, and in smaller degree from the rainfall; it appears probable also that ammonia and amide-like substances in the soil can be absorbed to some extent directly, without previous nitrification. The old observation that the nitrates in the soil will not account for all the nitrogen in a leguminous crop, and that such crops are not benefited by the application of nitrogenous manures to the same extent as are other crops, points to the conclusion that legumes have some exceptional source of nitrogen at their disposal. The discovery on the roots of these plants of tubercules containing organisms which appear to be in *symbiosis* (*σύν, together with; βίος, life*) with the plant, and to transform nitrogen, either from organic matter, or from the atmosphere, into nitrogenous compounds which can be absorbed by the roots, and the discovery that inoculation with some soil which is productive for legumes will render fertile one previously barren for such growth, are recent results of this interesting and important inquiry.

The sulphur and phosphorus are derived by the plant from sulphates and phosphates in the soil, while the other constituent elements are also derived from the mineral matter of the soil.

It is thus seen that the plant takes up its elements in a highly oxidised condition, and that the chemical tendency of vegetables is to reduce to a lower state of oxidation the substances presented in their food, whilst animals exhibit a reciprocal tendency to oxidise the materials on which they feed.

Soil is disintegrated rock, so that its composition will depend largely on the nature of the rock. To be fertile it must contain all the elements essential for plant growth (save carbon) in a condition available for absorption by the roots. Rarely more than 1 per cent. of the soil is in such a condition, the rest serving to support the plant mechanically, and becoming slowly available by the process of weathering (p. 128), which is much aided by ploughing, draining, and the various other operations of the farm.

The chief constituents of a soil are sand, clay, carbonate of lime, and humus. The proportion which these bear to each other greatly influences the physical properties of the soil, and consequently its fertility and cost of working. It is also closely connected with the *absorptive power* of the soil, or its capability of fixing fertilising matter; thus, humus retains the all-important ammonia, while the hydrated silicates, including clay, fix potash and phosphoric acid, from any solution containing these which may filter through the soil.

The first three of the above constituents need no comment here. *Humus* is the name applied to the organic matter in the soil; it consists of the brown and black substances resulting from the decay of previous vegetation. Sodium carbonate dissolves this brown humus to a brown solution, from which an acid precipitates

a brown substance having a faintly acid reaction, and therefore termed *ulmic* acid (*ulmus*, an elm); according to some, the humus contains a portion insoluble in sodium carbonate, to which the name *ulmin* has been given. Black humus yields by the same treatment *humic* acid and *humin*. Two other acids, *crenic* and *apocrenic*, the former convertible into the latter by oxidation, have also been obtained from the humus, and these have been found in mineral waters. All these substances are of ill-ascertained composition.

The humus is the store of nitrogenous matter, which, by slow nitrification, becomes available for the plant.

When a soil comes under tillage, the crops raised upon it are consumed by animals, and often removed to a distance, so that the mineral food and nitrogen contained in the soil are by degrees exhausted, and unless these are restored the soil becomes barren. To restore its fertility is the object of *manuring*, which consists in adding to the soil substances which shall serve directly as plant-food, or shall so modify by chemical action some material already present in the soil as to convert it into an available form. These two objects are often attained by one and the same manure.

Manures either supply all the necessary plant-foods—when they are termed *general* manures—or they supply some food which is especially wanting to enable the plant to flourish, and make use of food already existing in the soil. or perhaps to excite rapid growth at a critical period of its existence, when it is most sensitive to attacks of insects or vicissitudes of weather. Such are termed *special* manures.

Nitrogen, phosphorus, and potassium are the plant foods which are most rapidly exhausted and most generally needed. A general manure is accordingly valued by its content of these three elements, regard being had to the condition in which they exist; for, if they are soluble, they will be more rapidly and thoroughly distributed through the soil, thus becoming immediately available as food; if, on the other hand, they are in a condition not so available, the immediate benefit of the manure will be smaller, but it will last over a longer period, the constituents becoming soluble in the course of time.

The various manures can receive but short notice here. Of general manures the most valuable is *farm-yard manure*, consisting of the solid and liquid excrement of the farm stock, together with the litter used to absorb the liquid. Its value will be controlled by the quality and quantity of this litter; by the nature of the animals; the richness of their food in N, P_2O_5, and K_2O; whether they are in active work, in which case as much N, P_2O_5 and K_2O is voided as is consumed in the food; or being fattened, milked, or shorn, in which case some of the N, P_2O_5, and K_2O will be stored in the carcase or removed as milk or wool. But its value is most affected by its after-treatment. If it be stacked, exposed to rain, and the drainings not preserved, much soluble N, P_2O_5, and K_2O will be lost, which is not the case if it be spread directly on the land. Fresh farmyard manure in a heap rapidly becomes *rotten*, fermenting and losing much carbon as carbon dioxide and marsh gas, but very little nitrogen. It thus becomes more valuable, as it is less weighty when rotten and contains more of its N and P_2O_5 in a soluble condition. Rotten manure contains on an average 70 per cent. H_2O, 2.7 per cent. *true* ash, 0.6 per cent. N, 0.3 per cent. P_2O_5, and 0.5 per cent. K_2O.

Seaweed is allowed to have a manurial value approaching that of farmyard manure.

Guano (Peruvian), the dried excrement of sea-birds, contains, when it has been deposited in sheltered places, ammonium urate and other ammonium salts and nitrogenous matter (equivalent in all to 12 per cent. N); and the presence of calcium phosphate (26 per cent.) and small quantities of potassium salts render this variety a valuable general manure. If, however, the guano has been deposited in exposed places (Mejillones), its nitrogen has been lost, and it becomes a special *phosphatic* manure, containing about 70 per cent. of calcium phosphate.

Animal refuses of various kinds form general manures, valuable chiefly for their N, and vegetable matters will of course restore to the soil those mineral constituents which they have previously removed. *Rape cake*, the compressed refuse of the colza-oil factory, is a general manure of this kind. *Green manuring* has a special value, as it consists in keeping covered with vegetation soil which would otherwise be left fallow (and lose by drainage), and then ploughing-in the crop; as this is generally a deep-rooted one, mineral constituents and nitrogen are thus brought up from the *subsoil* and left in a quickly available form in the surface soil for the use of shallower-rooted crops.

Special manures supply either nitrogen, phosphorus, potassium, or calcium, and less frequently sulphur, chlorine, and magnesium.

The term *nitrates* as applied to manure usually implies sodium nitrate, the potassium salt being too expensive for use. *Sodium nitrate* supplies nitrogen in a very soluble, and therefore readily available, form, stimulating rapid growth. Its solubility renders it less effective in wet weather, as it is then washed through the soil; for the same reason, it is best applied as a *top-dressing* after growth has begun. As the sodium is not taken up by the crop, it partly remains in the soil as sodium carbonate and silicate, and tends to render it stiff. *Ammonium sulphate* also supplies nitrogen, but is less rapid in its action, and better fitted for wet weather than is nitrate. The ammonia rapidly undergoes nitrification, and the nitric acid formed combines with the lime in the soil. The sulphuric acid, not being used by the plant, also combines with the lime. Both these lime salts tend to get washed away, so that this manure is liable to remove lime from the soil. Diluted *gas liquor* is sometimes used as a manure on account of its ammonia. *Soot* owes its chief value to its 1 or 2 per cent. of ammonia.

Bones are of value for their phosphates (50 per cent.) and their nitrogen (3.5 per cent.); they are slow in action, and last long. Bone ash and mineral phosphates (coprolites, &c.), all of which contain no nitrogen, are occasionally used finely ground, but are generally employed for making *superphosphate* (p. 334). This most important manure is valued by the amount of monocalcium phosphate which it contains, though the manufacturer insists on this being calculated into tricalcium phosphate and then called "soluble phosphate" or "phosphate rendered soluble." For this soluble constituent, which should average 18 to 20 per cent. in a mineral superphosphate, is rapidly spread through the soil by the rain, and is there reconverted into phosphates which are insoluble in pure water, but are very finely divided, and thus easily soluble in carbonic acid, and available as food. *Dissolved bones* have been partially converted into superphosphate by treatment with sulphuric acid, and of course contain nitrogen. *Basic slag*, or *Thomas* or *Thomas-Gilchrist slag* (p. 410), is now employed as a manure on account of its phosphorus; it must be used in a very fine state of division. It contains 14 to 19 per cent. of P_2O_5, chiefly as the compound $4CaO.P_2O_5$, which is more soluble in saline solutions than is $3CaO.P_2O_5$.

Potassium is supplied in *kainit* (p. 311), which contains 13 to 14 per cent. K_2O. Other sources of this element are *carnallite*, *wood ashes*, *beet-sugar refuse*, and the *suint* or *yolk* of raw wool.

Lime as used by the agriculturist includes chalk, caustic lime, and slaked lime. It is more often employed for attacking the constituents of the soil than as a direct plant-food, there generally being enough in the soil for that purpose. Lime neutralises organic acids in the soil, sweetening it, and hastens the decay of organic matter, rendering the N available and furnishing CO_2 as a solvent for minerals. Its action on minerals is specially serviceable for decomposing injurious iron compounds and the felspars, rendering the K_2O of these latter available. Some limestones, and all shells, contain small quantities of P_2O_5, itself valuable.

Common salt is chiefly of value for its chemical action on the soil and for destroying weeds and pests. Sodium chloride is always brought down in small quantity from the air by the rain.

Gypsum and *magnesium sulphate* are occasionally used for a supply of sulphur.

616. In some cases fertility is restored to an apparently exhausted soil, without the addition of manure, by allowing it to lie *fallow* for a time, so that, under the influence of air, moisture, and frost, such chemical changes may occur in it as will again replenish it with food available for the crops. It is not even necessary in all cases that the soil should be altogether released from cultivation; for, even though it may refuse to feed any longer one particular crop, it may furnish an excellent crop of a different description, and, what is more remarkable, it may, after growing two or three different crops, be found to have regained its power of nourishing the very crop for which it was before exhausted. Experience of this has led to the adoption of a system of *rotation of crops*, by which a soil is made to yield, for example, a crop of barley, and then successive crops of clover, wheat, turnips, and barley again.

The possibility of this rotation is partly accounted for by the difference in the mineral food removed by different crops; thus, turnips and clover require much potash and lime, while wheat and barley require much phosphoric acid, so that

in alternating the turnips and clover with the wheat and barley, there may be sufficient time for some of the locked-up phosphoric acid of the soil to become available as food.

Moreover, the farm crops appear to differ in their capacity for feeding on the mineral substances present in the soil; thus, there may be phosphoric acid in a soil which would be available for wheat, but perfectly useless for turnips, which are for this reason always greatly benefited by manuring with superphosphate. Again, cereal crops are more benefited by application of nitrates than are most other crops.

An explanation of this is afforded by our knowledge of the difference in the depth to which the roots of various crops are capable of penetrating into the soil, and consequently of drawing a supply of food from the subsoil. The benefit of rotation is also partly to be accounted for in this way. For where the residue of the preceding deep-rooted crop is allowed to remain on the land, the surface soil will become enriched with food collected from the subsoil, and thus rendered available for the shorter-rooted crop when the residue is ploughed up. At the same time the opening up of the soil to different depths, caused by the differently penetrating roots, prevents the formation of the hard layer, or *pan*, which generally forms at the limit of the roots if the same crop be grown continually.

617. Our knowledge of the chemical operations occurring in the plant, and resulting in the elaboration of the great variety of vegetable products, is very slight indeed. We appear to have sufficient evidence that starch and sugar, for example, are constructed in the plant from carbonic acid and water, and that albuminoids result from the interaction of the same compounds, together with nitric acid, or ammonia, and certain sulphates and phosphates; but the intermediate steps in these conversions are as yet unknown.

All seeds contain starch or fat (or both), albuminoids, and mineral matters, these being provided for the nourishment of the young plant till its organs are sufficiently developed to enable it to procure its own food from the air and soil. The necessary conditions for germination are a suitable temperature (best at 28° to 34° C.), the presence of free oxygen, and moisture. It is to obtain this last that the seed is buried, light or darkness having little or no effect. The seed absorbs water and oxygen and evolves carbon dioxide; since the albuminous constituents are the most changeable substances present, it is probably these which undergo oxidation, part forming diastase, which excites the conversion of insoluble starch into soluble starch and sugar; some of the albuminoids at the same time become soluble amides. The water absorbed dissolves these altered substances and the mineral matters, forming the sap to nourish the embryo. The seed swells, and the integument bursts, the *radicle* growing first and then the *plumule;* the former develops into the root, which absorbs the mineral constituents and nitrogen in aqueous solution from the soil, while the latter, as the sap ascends, develops the leaves, the sugar of the sap becoming converted into cellulose for the purpose. Chlorophyll is then developed, and the decomposition of carbon dioxide and assimilation of carbon begins. As the roots act more quickly than the leaves, the young plant is relatively richer in mineral constituents and nitrogen than is the mature plant. The assimilation of carbon and decomposition of carbon dioxide proceed only in light, the volume of oxygen evolved being equal to that of the carbon dioxide absorbed,* so that the formation of cellulose might be regarded as occurring directly by the action of the carbon dioxide on the water of the sap, thus :—$6CO_2 + 5H_2O = C_6H_{10}O_5 + O_{12}$. The compounds, whatever they may be, that are formed by the assimilating process are altered and rendered soluble by a process of oxidation known as *metabolin*, accompanied by evolution of carbon dioxide—a veritable respiration, in fact, which goes on in light or dark, though in the light the evolved carbon dioxide is masked by the larger evolution of oxygen. *Osmosis* is concerned in the passage of the soluble matters from cell to cell.

By growing plants in water in which one particular constituent element is contained in very small proportion or is absent, it has been ascertained that potassium is concerned in the formation of starch and other carbohydrates; calcium in the formation of cellulose; iron in the formation of chlorophyll; chlorine in the

* It has been suggested that formic aldehyde is first produced, $CO_2 + H_2O = CH_2O + O_2$, and that this is subsequently polymerised to glucose, $C_6H_{12}O_6$. The recent production of acrose from formic aldehyde (p. 728) supports this view.

translocation of starch; phosphorus, sulphur, and nitrogen in the formation of albuminoids. The mission of calcium is also shown by the fact that wheat has a tendency to *lay* or *lodge* where the soil is poor in this element.

In annual plants the formation of seed is carried on at the expense of the rest of the plant, which becomes exhausted, starch and albuminoids being transferred to the seed. In biennial and perennial plants the advent of autumn is accompanied by a transference of food from the stem and leaves to the roots, tubers, or pith, to form a basis for growth next spring, exhaustion and death occurring in the case of biennial plants at seed-time, and the rotation recurring in the case of perennials.

618. With respect to the ripening of fruit, we know a little more concerning the chemical changes which it involves. Most fruits, in their unripe condition, contain cellulose, starch,* and some one or more vegetable acids, such as malic, citric, tartaric, and tannic, the last being almost invariably present, and causing the peculiar roughness and astringency of the unripe fruit. The *characteristic* constituent of unripe fruits, however, is *pectose*, a compound of carbon, hydrogen, and oxygen, the composition of which has not been exactly determined. Pectose is quite insoluble in water, but during the ripening of the fruit it undergoes a change induced by the vegetable acids, and is converted into *pectin* ($C_{32}H_{50}O_{32}$), which is capable of dissolving in water, and yields a viscous solution. As the maturation proceeds, the pectin itself is transformed into *pectic acid* ($C_{16}H_{22}O_{16}$) and *pectosic* acid ($C_{32}H_{46}O_{31}$), which are soluble in boiling water, yielding solutions which gelatinise on cooling. It is from the presence of these acids, therefore, that many ripe fruits are so easily convertible into jellies.

Whilst the fruit remains green, its relation to the atmosphere appears to be the same as that of the leaves, for it absorbs carbon dioxide and evolves oxygen; but when it fairly begins to ripen, oxygen is absorbed from the air and carbon dioxide evolved, whilst the starch and cellulose are converted into sugar under the influence of the vegetable acids (p. 726), and the fruit becomes sweet. The conversion of starch and cellulose ($C_6H_{10}O_5$) into sugar ($C_6H_{12}O_6$) would simply require the assimilation of the elements of water, so that the absorption of oxygen and evolution of carbon dioxide are probably necessary for the conversion of the tannic and other acids into sugar. For example—

$$\underset{\text{Tannic acid.}}{C_{14}H_{10}O_9} + H_2O + O_{12} = \underset{\text{Fruit-sugar.}}{C_6H_{12}O_6} + 8CO_2.$$

$$\underset{\text{Tartaric acid.}}{3C_4H_6O_6} + O_3 = C_6H_{12}O_6 + 3H_2O + 6CO_2.$$

When the sugar has reached its maximum, the ripening is completed; and if the fruit be kept longer, the oxidation takes the form of ordinary decay.

A change in composition, similar to that caused by ripening, is effected by cooking the unripe fruit.

619. The scheme of natural chemistry would not be complete unless provision were made for the restoration of the constituents of plants, after death, to the atmosphere and soil, where they might afford food to new generations of plants. Accordingly, very shortly after the death of a plant, if sufficient moisture be present, the spores of ferments acquired from the air begin to develop, the changeable nitrogenised (albuminous) constituents begin to putrefy, and the change is communicated to the other parts of the plant, under the form of decay, so that the plant is slowly consumed by the atmospheric oxygen, its carbon being reconverted into carbonic acid, its hydrogen into water, and its nitrogen into ammonia, these substances being then transported in the atmosphere to living plants which need them, while the mineral constituents of the dead plants are washed into the soil by rain.

Moist wood is slowly converted by decay into humus. When it is desired to preserve wood from decay, it is impregnated with some substance which shall form an unchangeable compound with the albuminous constituents of the sap. Kreasote (p. 712) and corrosive sublimate (*kyanising*) are occasionally used for this purpose, the wood being made to imbibe a diluted solution of the preservative, either by being soaked in it or under pressure.

In *Boucherie's process* for preserving wood, the natural ascending force of the sap is ingeniously turned to account in drawing up the preservative solution. A

* Some doubt exists as to the presence of starch in fruit.

large incision being made around the lower part of the trunk of the growing tree, a trough of clay is built up around it, and filled with a weak solution of sulphate of copper, peracetate of iron, or calcium chloride. Even after the tree has been felled, it may be made to imbibe the preserving solution whilst in a horizontal position, by enclosing the base of the trunk in an impermeable bag supplied with the liquid from a reservoir. The impregnation of the wood with such solutions not only prevents chemical decay, but renders it less liable to the attacks of insects and the growth of fungi.

NUTRITION OF ANIMALS.

620. Between the chemistry of vegetable and that of animal life there is this fundamental distinction, that the former is eminently constructive and the latter destructive. The plant, supplied with compounds of the simplest kind—carbonic acid, water, and ammonia—constructs such complex substances as albumin and sugar; whilst the animal, incapable of deriving sustenance from the simpler compounds, being fed with those of a more complex character, converts them eventually, for the most part, into the very materials with which the constructive work of the plant began. It is indeed true that some of the substances deposited in the animal frame, such as fibrin, and gelatinous matter, rival in complexity many of the products of vegetable life; but for the elaboration of these substances, the animal must receive food somewhat approaching them in chemical composition. It is to this nearer resemblance between the food of animals and the proximate constituents of their frames, that we may partly ascribe the greater extent of our knowledge on the subject of the nutrition of animals, which is, however, far from being complete.

The *ultimate* elements contained in the animal body are the same as those of the vegetable, but the *proximate* constituents are far more numerous and varied.

The bones containing the phosphates and carbonates of calcium and magnesium together with gelatinous matter, require that the animal should be supplied with food which, like bread, contains abundance of phosphates, as well as the nitrogenised matter (gluten) from which the gelatinous substance may be formed. In milk, the food of the young animal, we have also the necessary phosphates, whilst the casein affords the supply of nitrogenous matters.

Muscular flesh finds, in the gluten of bread and the casein of milk, the nitrogenised constituent from which its fibrin might be formed with even less transformation than is required for the gelatinous matter of bone, since the composition of fibrin, gluten, and casein is very similar. The albumin and fibrin of the blood have also their counterparts of the gluten and casein of bread and milk, whilst all the salts of the blood may be found in either of these articles of food.

Bread and milk, therefore, may be taken as excellent representatives of the food necessary for animals, and the same constituents are received in their flesh diet by animals which are purely carnivorous, but the flesh contains them in a more advanced stage of preparation.

It is natural to suppose that the fat, which contains no nitrogen, should be supplied by those constituents of the food which are free from that element, such as the starch in bread, and the sugar and fat in milk.

Before the food can be turned to account for the sustenance of the body, it must undergo *digestion*, that is, it must be either dissolved or otherwise reduced to such a form that it can be absorbed by the blood, which it accompanies into the lungs to undergo the process of *respiration*, and thus to become fitted to serve for the *nutrition* of the various organs of the body, since these have to be continually repaired at the expense of the constituents of the blood.

The first step towards the digestion of the food is its disintegration effected by the teeth with the aid of the *saliva*, by which it should be reduced to a pulpy mass. The saliva is an alkaline fluid characterised by the presence of a peculiar albuminous substance called *ptyalin* (πτύω, *to spit*), which easily putrefies. The action of saliva in mastication is doubtless in great part a mechanical one, but it is possible that its alkalinity assists the process chemically, by partly emulsifying the fatty portions of the food. The ptyalin also acts as a ferment, converting starch into sugar. This disintegration of the food is of course materially assisted by the cooking to which it has been previously subjected, the hard and fibrous portions having been thereby softened.

The food now passes to the stomach, in which it r
temperature of the body (98° F.), in contact with
chemical agent in the digestive process. The gastr
the lining membrane of the stomach is an acid liq
and lactic acids. It is characterised by the prese
belonging to the albuminous class of bodies whicl
digest), and possesses the remarkable power of enab
presence, to dissolve such substances as fibrin anc
would resist the action of the acid alone for a great

An imitation of the gastric juice may be made by
brane of the stomach for some hours in warm very d
acid liquid thus obtained is capable of dissolving n
tained at the temperature of the body. The pepsir
of the pig and other animals is sometimes adminis
assist digestion.

The principal change which the food suffers by th
is the conversion of the fibrinous and albuminous co
(*peptones*); the starch is also partly converted into
fatty constituents are unchanged.

The food which has thus been partially digested
physiologists *chyme*, and passes thence into the com
(the *duodenum*), where it is subjected to the action
the *bile* and the *pancreatic juice*.

621. *Bile* consists essentially of a solution of two
and taurocholate of sodium. Both glycocholic and t
and do not neutralise the alkali, so that the bile has
Another characteristic feature of this secretion is th
which it contains. *Glycocholic acid* contains 67 per
cholic acid contains 01 per cent.

The special function of the bile in the digestion c
plained, but from its strongly alkaline reaction it do
it assists in the digestion of fatty substances.

The *pancreatic juice* is another alkaline secretion
containing a considerable quantity of albumin, and
ticular office in digestion appears to consist in prot
starchy portions of the food into sugar, though i
upon the fats, causing them to form an intimate
water, and partly saponifying them. The digestio
completed by the action of the *intestinal fluid* in th
through the intestines, so that when it arrives in
soluble matters have become converted into a thin m
has next to be separated mechanically from the inso
fibre, &c., which are excreted from the body.

This separation is effected in the small intestines
of vessels, one of which (the *lacteals*) absorb
tions of the food, and conveys them to the liver.
transferred to the right auricle of the heart. The
absorbs the digested fatty matters, and conveys the
into the subclavian vein, and thence at once into th

From the right auricle this imperfect blood passe
the heart, and is there mixed with the blood return
after having fulfilled its various functions in the sys
the usual dark brown colour of venous blood, is ser
of the heart, into the lungs, where it is distributed
of extremely fine vessels traversing the lungs in al
containing the inspired air so that the venous blo
are by very thin and moist membranes. Thereb
venous blood gives up the carbonic acid gas with w
by the oxidation of the carbon of the tissues in its p
acquires in return about an equal volume of oxyge
bright crimson arterial blood. In this state it return
whence it is conveyed by the arteries to the differ
elements of the tissues effected and suffered by
through the body is very imperfectly understood.

supply of the oxygen necessary to oxidise the components of the various organs, and thus to evolve the heat which maintains the body at its high temperature. The results of the oxidation of these organs are undoubtedly very numerous; among them we may trace carbonic, sulphuric, phosphoric, lactic, butyric, and uric acids, as well as urea and some other substances. The destroyed tissues must at the same time be renewed by the deposition, from the blood, of fresh particles similar to those which have been oxidised. In the course of the blood through the circulation, the above products of oxidation have to be removed from it—the carbonic acid by the lungs and skin—the sulphuric, phosphoric, and uric acids, and the urea, by the kidneys.

The various liquid secretions of the body, such as the bile, the saliva, the gastric juice, &c., have also to be elaborated from the blood during its circulation through the arteries, after which it returns, by the veins, to the heart, to have its composition restored by the matters derived from the food, and to be reconverted into arterial blood in the lungs.

When it is remembered that the body is exposed to very considerable variations of external heat and cold, a question occurs as to the provision made for maintaining it at its uniform temperature. This is effected through the agency of the fat which is deposited in all the organs of the body. Since fatty substances in general are particularly rich in carbon and hydrogen, their oxidation within the body would be attended with the production of more heat than that of those parts of the organs which contain much nitrogen and oxygen. Accordingly, when the body is exposed to a low temperature, a larger quantity of its fat is consumed by the oxidising action of the blood, and a corresponding increase occurs in the amount of heat evolved, thus compensating for the greater loss of heat suffered by the body in the cooler atmosphere. Of course, in cold weather, when more oxygen is required to maintain the heat of the frame, a larger quantity of that gas is inhaled at each breath, on account of the higher specific gravity of the air, in addition to which we have the quickened respiration which always attends exposure to cold. To supply this extra demand for carbon and hydrogen in cold weather, we instinctively have recourse to such substances as fat, starch, sugar, &c., which contain them in large proportion, and these aliments, free from nitrogen, are often spoken of as the *respiratory constituents* of food; whilst flesh, gluten, albumin, &c., which contain nitrogen, are styled the *plastic* elements of nutrition (πλάσσω, *to form*).

Bearing in mind that the food has a two-fold office—to nourish the frame and to maintain the animal heat—it will be evident that a judiciously regulated diet will contain due proportions of these nitrogenous constituents, such as albumin, fibrin, and casein, which serve to supply the waste of the organs, and of such non-nitrogenised bodies as starch and sugar, from which fat may be elaborated to sustain the bodily warmth.

Albuminoid ratio.—The proportion which these two parts of the food should bear to each other will, of course, depend upon the particular condition of existence of the animal. Thus, for a growing animal a larger proportion of the nitrogenised or plastic portion of food would be required than for an animal whose growth has ceased; and animals exposed to a low temperature would require more of the non-nitrogenised or heat-giving portion of the food.

Accordingly, we find that a man can live upon a diet which contains (as in the case of wheaten bread) 5 parts of non-nitrogenised (starch and sugar) to 1 part of nitrogenised food (gluten); whilst an infant, whose increasing organs require more nitrogenised material, thrives upon milk, in which this amounts to 1 part (casein) for every 4 parts of the non-nitrogenised portion (milk-sugar and fat). The inhabitants of cold climates consume, as is well known, much more oil and fat than do those of the temperate and hot regions.

An examination of the composition of different articles of food affords us an explanation of the custom which experience has warranted, of associating particular varieties of food. Thus, assuming as our standard of comparison the composition of bread, which contains one of nutritive to five of heat-giving matter, the propriety of eating potatoes (1 nutritive : 10 heat-giving) with beef (1 nutritive : 1.7 heat-giving), and rice (1 : 12.3) with mutton (1 : 2.7), will be appreciated.

All muscular or mental exertion is attended with a corresponding oxidation of the tissues of the frame, just as each movement of a steam-engine may be traced to the combustion of a proportionate quantity of coal under the boiler, and hence

such exertion both creates a demand for food, and quickens the respiration to obtain an increased supply of oxygen.

CHANGES IN THE ANIMAL BODY AFTER DEATH.

622. After the death of animals, just as after that of plants, a change occurs in some of the nitrogenous constitutents, attended by the development of living organisms of a very low order, and this change is soon communicated to all parts of the body, which undergoes a putrefaction or metamorphosis, of which the ultimate results are the conversion of the carbon into carbonic acid, the hydrogen into water, the nitrogen into ammonia, nitrous and nitric acids, and the sulphur into sulphuretted hydrogen and sulphuric acid. The mineral constituents of the animal frame then mingle with the surrounding soil, and are ready to take part in the nourishment of plants, which construct the organic components of their frames from the carbonic acid and ammonia furnished by the putrefaction of the animal, and then serve in their turn as sustenance for animals whose respiration supplies the air with carbonic acid gas and takes in exchange the oxygen eliminated by the plant.

The functions of the two divisions of animate nature are, therefore, perfectly reciprocal, and this relationship must be regarded as the foundation of economical agriculture. If it were possible to prevent the change of the atmosphere, it is quite conceivable that a perpetual succession of plants and animals could be raised upon a given farm, without any importation of food, provided that there was also no exportation. Or even, permitting an exportation of food, the succession of plants and animals raised upon the same land might be, at least, a very long one, if the solid and liquid excrement of the animals, to feed whom was the object of this exportation, were restored to the land upon which this food was raised. The explanation of this is, that the solid and liquid excrements of the animal contain a very large proportion of the mineral constituents of the soil, in the very state in which they are best fitted for the assimilation by the crop, and as long as the soil contains the requisite supply of mineral food, the plant can derive its organic constituents from the atmosphere itself.

Forasmuch, however, as the vegetable and animal food produced upon a farm is generally exported to feed the dwellers in towns, whose excrements cannot, without excessive outlay, be returned to the soil whence the food was derived, it becomes necessary for the agriculturist to purchase farm-yard manure, guano, &c., in order to prevent the exhaustion of his soil. A great manufacturing country, in which the majority of the inhabitants are congregated in very large numbers around a few centres of industry, at a distance from the land under tillage, is thus of necessity dependent for a considerable proportion of its food upon more thinly populated countries where manufactures do not flourish, to which it exports in return the produce of the labour which it feeds.

The parts of the frames of animals differ very considerably in their tendency to putrefaction. The blood and muscular flesh undergo this change most readily, as being the most complex parts of the body, whilst the fat remains unchanged for a much longer period, and the bones and hair will also resist putrefaction for a great length of time. The comparative stability of the fat is observed in the bodies of animals which have been buried for some time in a very wet situation, when they are often found converted almost entirely into a mass of *adipocere*, consisting of the palmitic and stearic acids derived from the fat.

When an animal body is thoroughly dried, it may be preserved unchanged for any length of time, and this is the simplest of the methods adopted for the preservation of animal food, becoming far more efficacious when combined with the use of some antiseptic substance, such as salt, sugar, spice, or kreasote. The preservative effects of salt and sugar are sometimes ascribed to the attraction exerted by them upon moisture, which they withdraw from the flesh, whilst spices owe their antiseptic power to the essential oils, which appear to have a specific action in arresting fermentative change, a character which also belongs to kreasote, carbolic acid, and probably to other substances which occur in the smoke of wood, well known for its efficacy in *curing* animal matter. Such substances are often called *anti-zymotic* bodies; carbolic, salicylic, benzoic, and boric acids are classed under this head.

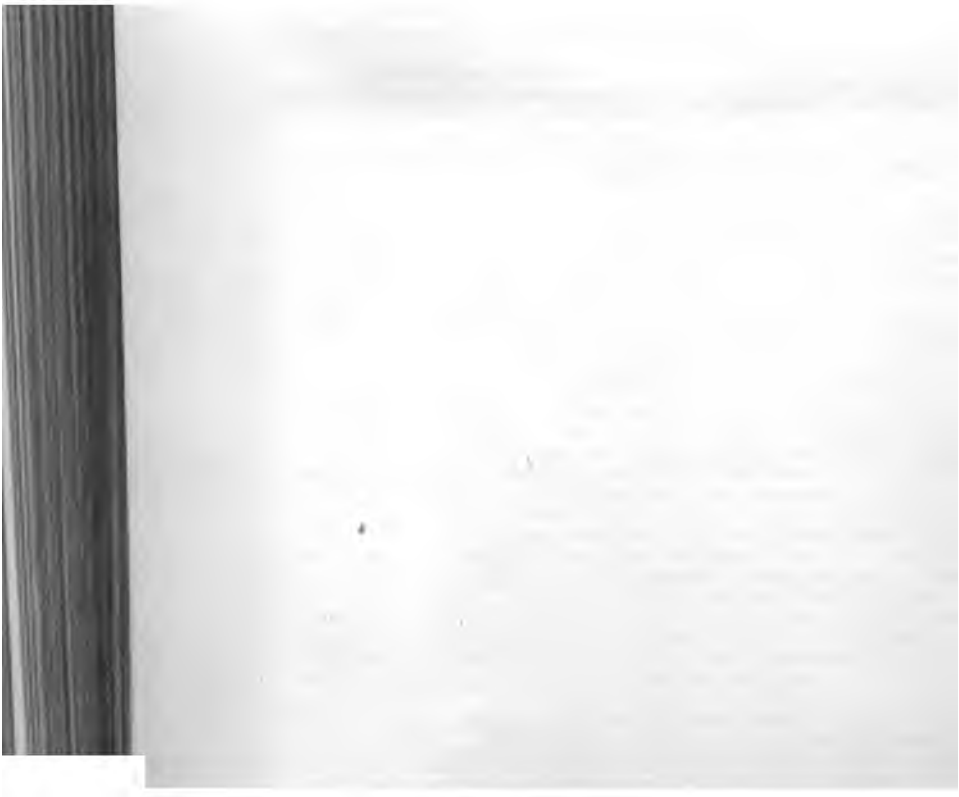
A process commonly adopted for the preservation of animal and vegetable food

consists in heating them with a little water in tin canisters, which are sealed air-tight as soon as the steam has expelled all the air, and if the organic matter be perfectly fresh, this mode of preserving it is found very successful, though, if putrefaction has once commenced, to ever so slight an extent, it will continue even in the sealed canister quite independently of the air.

Modern experiments have disclosed a great imperfection in our acquaintance with the conditions under which putrefaction occurs, and indicate the presence in the atmosphere of some minute solid particles which appear to be minute ova or germs, and have the power of inducing the commencement of this change. It has been found that milk, for example, may be kept for a very considerable period without putrefying, if it be boiled in a flask, the neck of which is afterwards loosely stopped with cotton wool, whilst, if the plug of cotton wool be omitted, the other conditions being precisely the same, putrefaction will set in very speedily.

Perfectly fresh animal matters have also been preserved for a length of time in that state, in vessels containing air which has been passed through red-hot tubes with the view of destroying any living germs which might be present, and such substances have been found to putrefy as soon as the unpurified air was allowed access to them.

The extremes of the scale of animated existence would appear to meet here. The highest forms of organised matter, immediately after death, serve to nourish some of the lowest orders of living germs, these helping to resolve the complex matter into the simpler forms of carbonic acid, ammonia, &c., which are returned to the atmosphere, the great receptacle for the four chief elements of living matter—carbon, hydrogen, nitrogen, and oxygen.



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*** *The names of minerals are printed in italics.*

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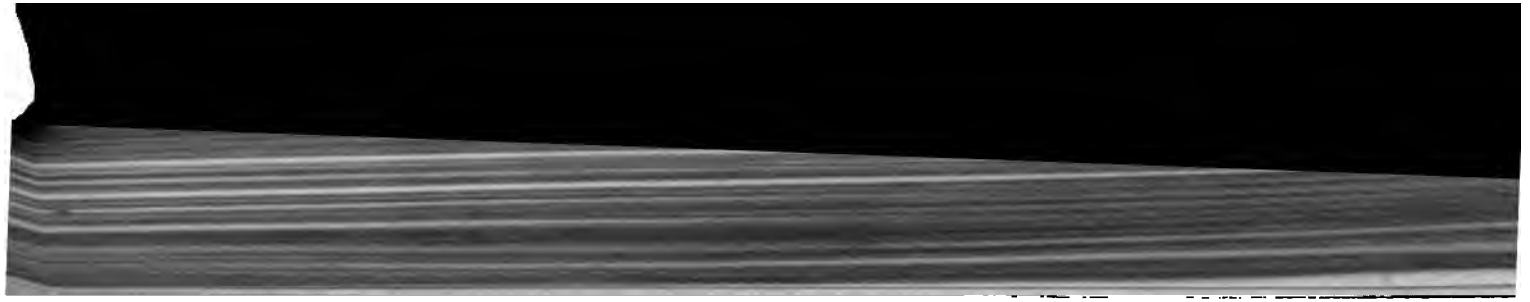

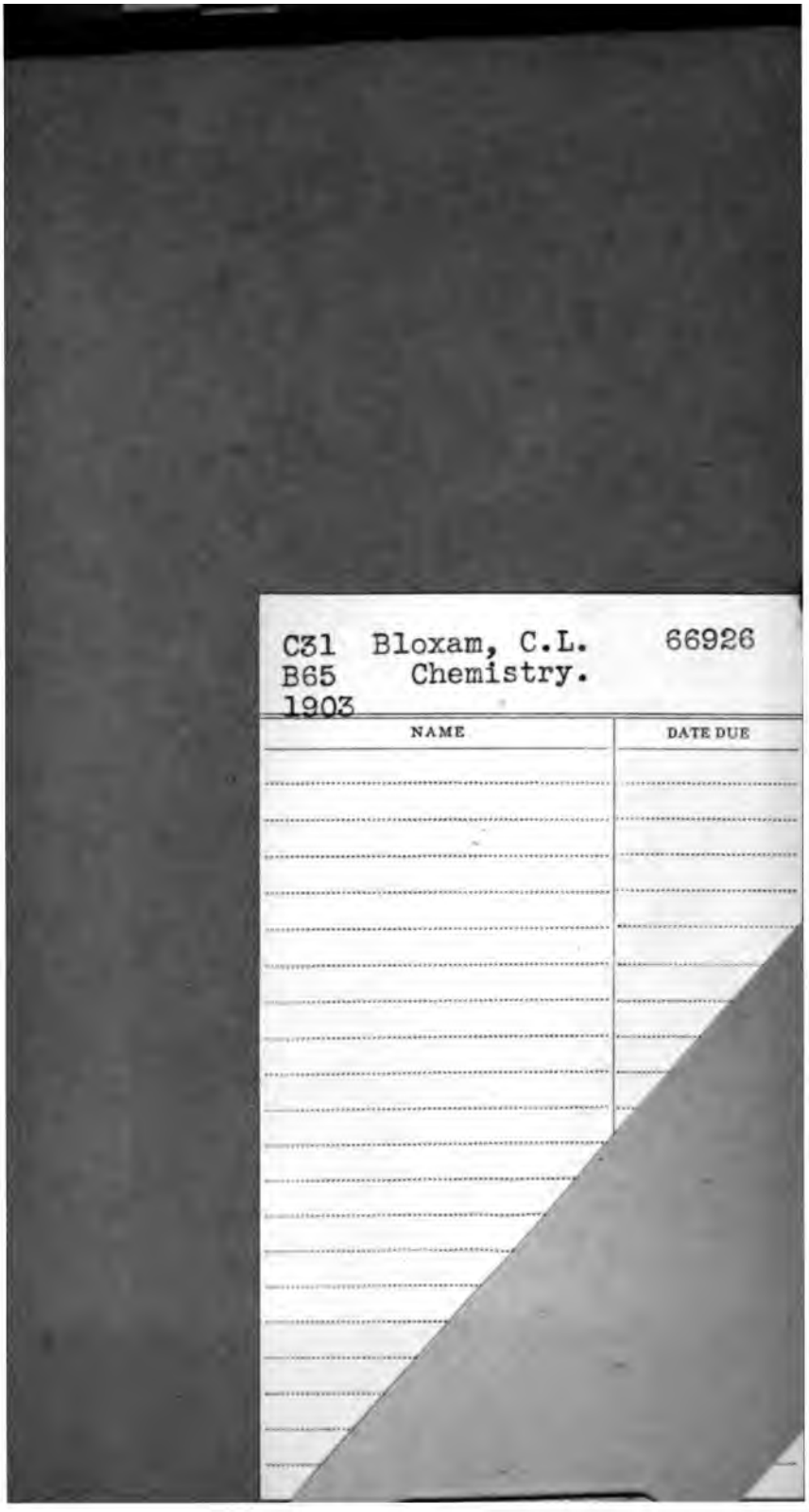
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